THE SYNTHESIS AND UTILIZATION OF LOW MOLECULAR WEIGHT OZONIDES FOR AIR REVITALIZATION

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of November 14, 1965

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NOTICE

This supplement, together with the interim report[1] of November 14, 1965, constitutes the final report in fulfillment of the requirements of NASA Contract NASw-559.

ACKNOWLEDGEMENT

The authors express their appreciation to Dr. V. Nacci and Mr. S. Huston of the Civil Engineering Department of the University of Rhode Island for graciously allowing the use of their R. L. Stone Differential Thermal Analysis unit. The assistance of Mr. H. P. Vaughn of the Mettler Instrument Co. in obtaining the DTA-TGA-DTG thermograms of several sodium superoxide and lithium peroxide samples is also gratefully acknowledged.

OBJECTIVE

The objective of the overall program covered by the contract is to synthesize and evaluate low molecular weight alkali metal ozonides, superoxides, and calcium superoxide for use as air revitalization materials.

The objective of the phase of the program covered in this report is to determine the thermal decomposition characteristics of sodium superoxide and lithium peroxide.

ABSTRACT

A study of the thermal stability of sodium superoxide, sodium peroxide, and lithium peroxide was conducted. The techniques of differential thermal analysis, thermogravimetry and differential thermogravimetry were used in evaluating the effects of metallic oxide and metallic-organic catalysts on the temperatures and rates of decomposition of these compounds. Results indicated that catalysts do not lower the thermal decomposition temperature but, in some cases, accelerate the rate of decomposition at a given elevated temperature. The effect of preconditioning sodium superoxide samples by exposure to humid atmospheres was also studied. Such conditioning lowers the decomposition temperature slightly. Isothermal kinetic data was also generated for a number of catalyzed systems. Magnetic susceptibility studies for calcium superoxides were extended to include measurements at temperatures ranging from -178 to 38°C.

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THE THERMAL DECOMPOSITION OF ALKALI METAL SUPEROXIDES AND PEROXIDES

1. INTRODUCTION

The experimental studies conducted during the periods covered by the subject contract were extended to investigate the thermal decomposition characteristics of sodium superoxide and lithium peroxide. Sodium peroxide was also included in these studies since it is formed as an intermediate compound in the course of the thermal decomposition of sodium superoxide.

The interim report presented the results of studies of the synthesis and chemical characterization of alkali metal superoxides, with particular emphasis on calcium superoxide. Calcium superoxide is attractive as an air revitalization material because the crusting problem common to alkali metal superoxide-water vapor reactions is not encountered. However, because calcium superoxide cannot be prepared in sufficiently pure form and because of the complexity of the reactions of this compound with carbon dioxide and water vapor, calcium superoxide is not yet competitive with alkali metal superoxides. It was concluded in the interim report, therefore, that sodium and potassium superoxides offered the greatest potential for practical applications at the present time.

As an alternative to the alkali metal superoxide-water vapor canister reaction for back-pack type applications, an investigation of the thermal decomposition characteristics of sodium superoxide and lithium peroxide to produce oxygen was proposed. A reactor to supply oxygen based on the thermal degradation of these materials would not require water vapor, would be small, compact, easy to control, and probably suitable for "on-off" type applications. In addition, the sodium or lithium oxide products formed by the thermal decomposition of the corresponding superoxide are,themselves, excellent carbon dioxide scrubbers. Thus an efficient and reliable space-suit back-pack unit can be envisioned which could operate without the use of water.

From an engineering point of view, the alkali metal superoxides are thermally stable, i.e., at normal operating temperatures, the dissociation pressure of oxygen is extremely low for the conversion of the superoxide to the oxide and oxygen. Nevertheless, reasonable temperatures are attainable at which these decompositions will occur quantitatively. Potassium superoxide has been reported to decompose to the oxide and oxygen at about 280-300°C.[2] On the other hand, Shechter and Shakely [3] have noted that sodium superoxide is "not thermally stable at 100°C." At this temperature, however, their early studies indicate that the rate is very slow. Petrocelli[4] has shown that the use of pretreatment techniques or the use of a suitable catalyst can cause the thermal degradation of potassium superoxide to proceed to completion at 150°C. Thus, it was felt that similar techniques would lower the decomposition temperatures of sodium superoxide to an operable region.

Lithium peroxide is another air revitalization compound of interest because it too will decompose thermally to the oxide and oxygen. Markowitz has noted that the decomposition occurs at 300°C but is dependent upon surface area.[5]

A study of the thermal decomposition characteristics of sodium superoxide and sodium and lithium peroxides was undertaken to determine:

1. the temperatures at which the pure compounds decompose to evolve oxygen, employing thermogravimetric analysis and differential thermal analysis techniques;
2. the effect of pretreatment of the pure samples on the decomposition characteristics;
3. the effect of catalysts on the temperatures of decomposition;
4. the rates of oxygen evolution under isothermal conditions;

The results of these studies are presented and discussed in this report along with additional magnetic susceptibility data for calcium superoxide which was obtained during the extended work period.

2. RESULTS OF EXPERIMENTAL STUDIES

2.1 DIFFERENTIAL THERMAL ANALYSIS, THERMOGRAVIMETRY, AND DIFFERENTIAL THERMOGRAVIMETRY

2.1.1 Introduction

A number of analytical techniques are available by which the characteristics of a material subjected to uniform heating rates may be examined. In this research, three complementary techniques were employed in studying the thermal behavior of sodium superoxide, lithium peroxide and sodium peroxide. These methods were differential thermal analysis (DTA), thermogravimetric analysis (TGA) and differential thermogravimetry (DTG).

When a material is subjected to a uniform heating rate, thermal gradients are established within the material. If the sample should undergo a chemical or physical change while being heated, the normal thermal gradients are altered and a measurable change in the heat content of the sample results. These heat changes are the basis for the differential thermal method. In DTA, the test sample is placed in a heating block adjacent to an inert reference material such as alumina. The difference in the temperatures of the sample and the reference is then measured by means of a differential thermocouple as the two materials are simultaneously heated. If the sample gives off heat (as in crystallization) or absorbs heat (as in melting), then a measurable difference in temperature between the sample and reference material will occur. A plot of this Δt versus temperature, T, is known as the DTA thermogram.

The use of DTA methods allows the detection of all transitions involving heat changes which a sample undergoes under thermal agitation. Further, the nature of the transition (i.e. exothermic or endothermic) is also immediately known. Unless additional information is available, however, it is difficult to distinguish physical changes, such as melting or solid phase transitions, from chemical changes, such as decomposition or oxidation. For this reason, DTA data is most often supplemented by some other analytical technique. The most commonly employed complementary method is thermogravimetry. Here the changes in the weight of a material are recorded as a function of the temperature. Combining the two methods then, it is possible to distinguish chemical (weight) changes from physical transitions and, therefore, to identify to a great extent the nature of the processes induced in the material by heating.

A third method, employed to a limited extent only in this work, was differential thermogravimetry (DTG). DTG data is derived from TGA results and furnishes the first derivative of the TGA curve (i.e. dw/dt as a function of the temperature, t). This method, therefore, provides information concerning the rates of the processes occurring at various temperatures.

2.1.2 Experimental Program

One of the objectives of this extension was the evaluation of the effects of a number of metallic oxide catalysts on the thermal stability of sodium superoxide, sodium peroxide, and lithium peroxide. Because of the large number of tests required for such an evaluation program, it was necessary to establish some method of screening the various systems and conditions. This was accomplished according to the scheme outlined in Figure 1. An appropriate catalyst level was first established by running DTA thermograms on sodium superoxide samples containing three different levels of copper oxide catalyst. The thermograms were then compared with that of pure NaO_2. Since in the case at hand there was little difference noted in the curves, a 10% catalyst concentration was arbitrarily selected for testing. Using this catalyst concentration, a large number of superoxide samples containing different metallic oxides were prepared and analyzed, using the DTA method. The oxides evaluated are listed in Table I.

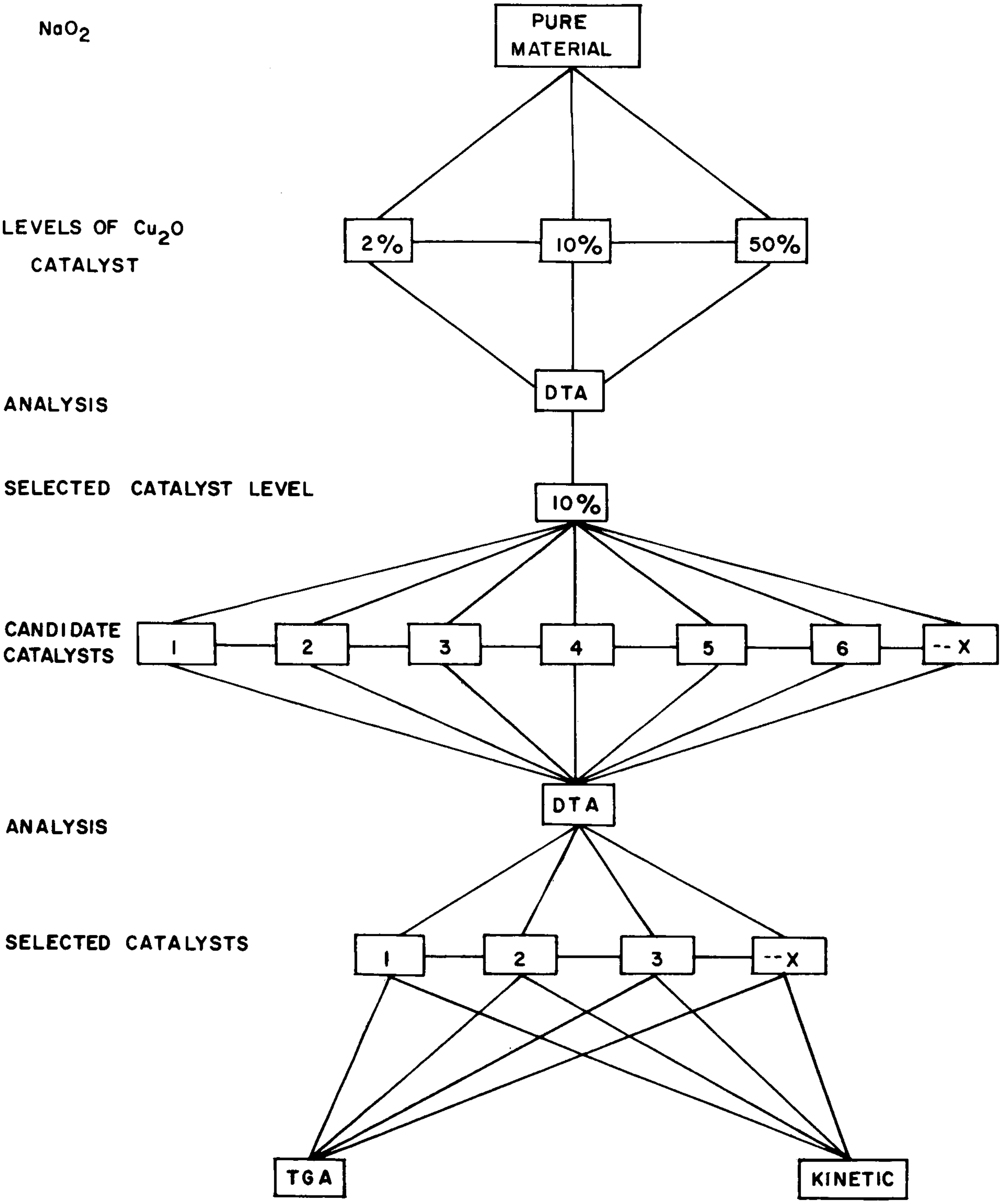


FIGURE 1 SCREENING OF METALLIC OXIDE CATALYSTS BY DTA

TABLE I

METAL OXIDES INVESTIGATED FOR CATALYTIC EFFECTS ON THE THERMAL DECOMPOSITION OF SODIUM SUPEROXIDE

1.	Cuprous Oxide	(Cu_2O)
2.	Vanadium Oxide	(V_2O_5)
3.	Vanadium Oxide	(V_2O_3)
4.	Palladium Oxide	(PdO)
5.	Titanium Oxide	(TiO_2)
6.	Nickel Oxide	(NiO)
7.	Iron Oxide	(Fe_2O_3)
8.	Manganese Dioxide	(MnO_2)
9.	Iron Oxide	(Fe_3O_4)
10.	Silver Oxide	(Ag_2O)
11.	Cadmium Oxide	(CdO)
12.	Polymeric Copper Phthalocyanine (1)	
13.	Polymeric Copper Phthalocyanine (2)	

The two metallo-organic compounds listed were also investigated as catalysts in this phase of the work. These polymeric copper phthalocyanines were synthesized by the condensation of pyromellitic dianhydride with urea, boric acid and cuprous chloride.[6]

Based on the DTA results, the systems were again screened, and selected catalysts were subjected to TGA and/or isothermal kinetic studies.

In addition to evaluating the above-mentioned catalysts, a portion of the effort was devoted to a study of the catalytic effects of absorbed water vapor on the thermal stability of sodium superoxide. Samples were exposed to 100% humidity for various periods of time and then analyzed by DTA. A difficulty which interfered with this approach was the fact that the water absorption occurred almost exclusively on the sample surface, causing a "crusting" of the top of the sample. This crusting prevented the water from penetrating into the sample and resulted in reactions occurring only on the surface. To overcome this difficulty, the samples were thoroughly mixed after exposure and prior to analysis.

2.1.3 Materials

The sodium superoxide used in this work was obtained from the Mine Safety Appliances Company, and was purported to be of ca. 98% purity. Lithium peroxide was obtained in purities of ca. 98% from the Foote Mineral Company; Sodium peroxide was a certified A.C.S. grade chemical assaying at 94.09%. Metallic oxides were reagent grade chemicals and were used as supplied without further purification or treatment.

The polymeric copper phthalocyanine catalysts were synthesized according to the following procedure:

Compound 1: Pyromellitic dianhydride (5g., 0.02M), phthalic anhydride (10g., 0.07M), urea (20g., 0.33M), cuprous chloride (1.5g., 0.02M), and catalytic amounts of boric acid were intimately mixed and placed in a glass pressure bottle. The dry mixture was heated at 200-220°C for five hours. At the end of this time, the porous green-blue solid was removed, washed successively with large volumes of water, ammonium hydroxide solution (10% conc.), water, dilute hydrochloric acid, water, and was dried. The crude material was treated with dimethylformamide to separate the product from any monomeric copper phthalocyanine which might have formed. The dark blue residue was identified as a phthalocyanine by means of infrared and elemental analyses.[6]

Compound 2: This material was prepared according to the above procedure with the exception that phthalic anhydride was omitted from the reactant mixture. The product was green and was slightly soluble in dimethylformamide.

2.1.4 DTA Studies

The differential thermal analysis data described in this report were obtained using a R.L. Stone apparatus model DTA-11M. The instrument was equipped to provide a number of dynamic atmospheres in the analysis. Dry air, however, was chosen here, because it was felt that it was the atmosphere which would be encountered in the practical application of these superoxides. The temperature program rate was maintained at 10 degrees per minute and the reference material was Alundum.

Because of the hygroscopic nature of the materials studied, it was necessary to take unusual precautions when loading the DTA sample holder to prevent contamination of the sample by atmospheric moisture. This was accomplished by fashioning a portable glove-bag out of polyethylene. The bag was positioned over the sample holder, a desiccant and the sample to be analyzed were placed inside, and the entire enclosure was sealed with adhesive tape. Figure 2 is a schematic design of the furnace assembly of the Stone apparatus and Figure 3 shows the improvised dry-bag in place. After the sample holder was loaded, the bag was removed. At the end of each run, the glove-bag was replaced, and the furnace, thus enclosed, was allowed to cool in the presence of the desiccant.

2.1.5 Thermogravimetric Analysis

In order to carry out the TGA studies, a Mettler automatic balance was converted into a thermobalance. A hole was drilled in the bottom of the balance, a converter attachment was adjoined to the bottom of the pan, and rhodium-plated jeweler's chain and sample holder were attached. The sample holder was suspended in a Hoskins electric furnace which was placed in a completely enclosed chamber. The entire chamber, therefore, could be purged with dry nitrogen prior to operation. A thermocouple was placed midway in the oven and the oven temperature was increased at a uniform rate by means of a Leeds-Northrup Speedomax temperature programmer. A schematic diagram of the thermobalance is given in Figure 4. During operation, the temperature was recorded manually every two minutes by means of a potentiometer.

2.1.6 Simultaneous DTA-TGA and DTG

Although DTA and TGA results are complementary techniques, it is not always possible to obtain exact correlations of data if

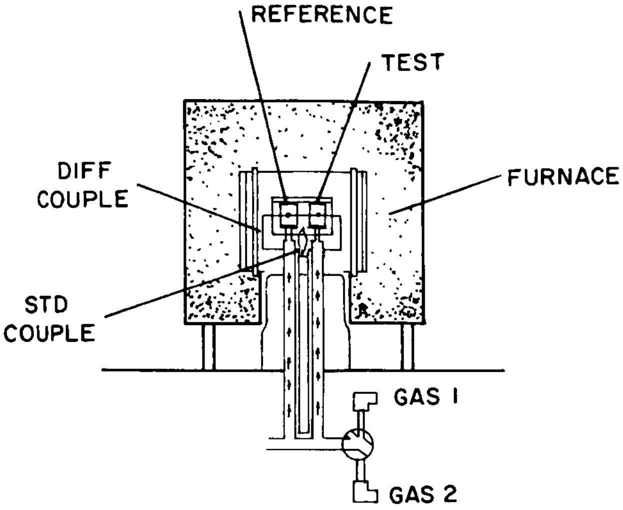


FIGURE 2 FURNACE ASSEMBLY OF R.L. STONE DTA-11M

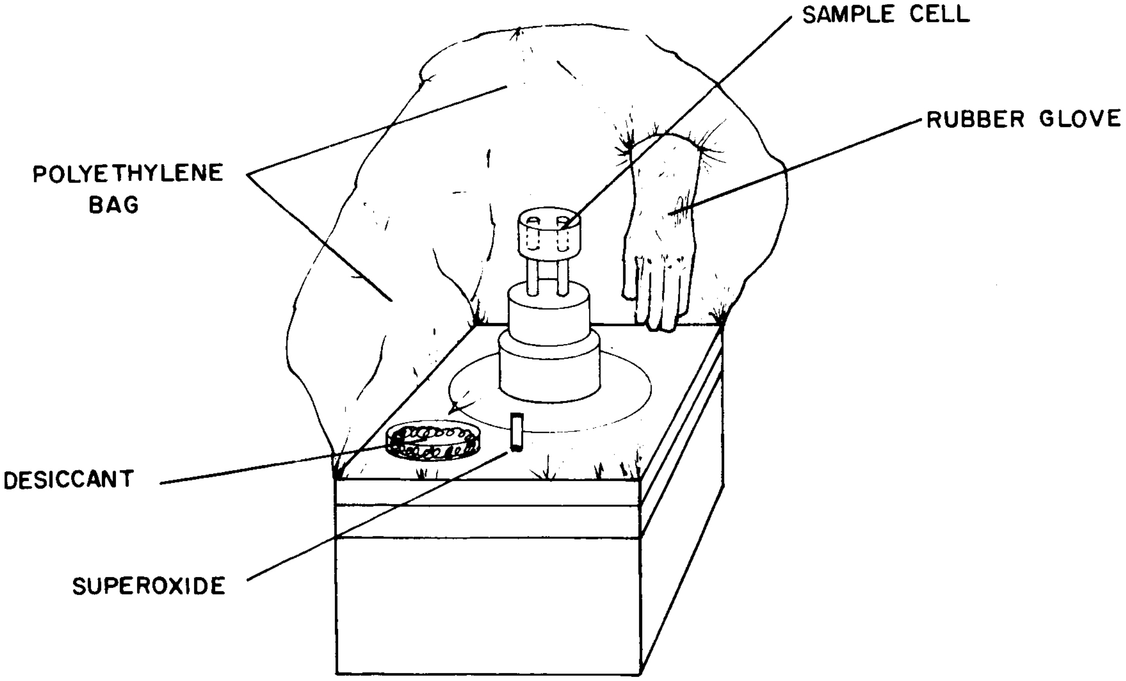


FIGURE 3 DRY-BAG ASSEMBLY FOR LOADING DTA SAMPLES

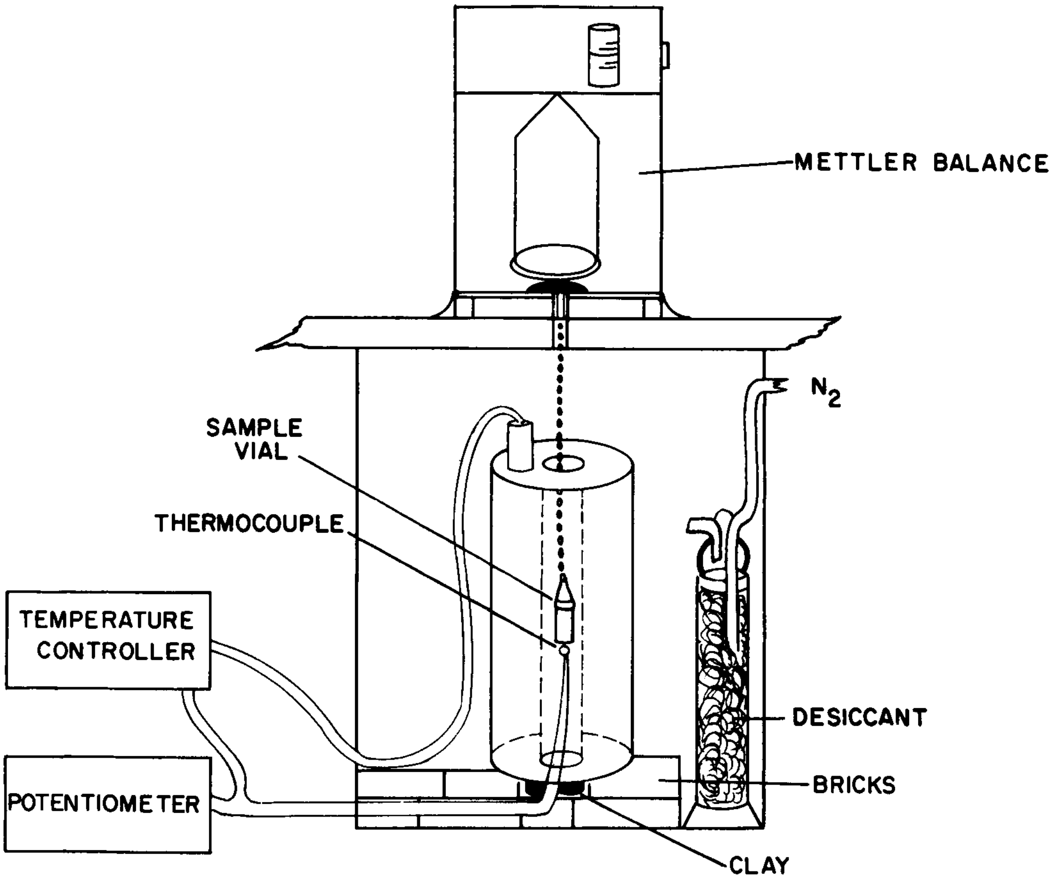


FIGURE 4 CONVERTED METTLER BALANCE

the experiments are performed on different instruments. For this reason, it is desirable to conduct simultaneous DTA-TGA experiments. A few selected samples, therefore, were submitted to the Mettler Instruments Laboratory in Sträfa, Switzerland, for evaluation on their recording thermoanalyzer. This instrument yields DTA, TGA and DTG data simultaneously under identical experimental conditions.

2.1.7 Results of DTA Studies

a. Pure NaO_2

The DTA thermograms obtained in this phase of the work are given in Figures 5 through 13. Examination of the thermogram for pure sodium superoxide (Figure 5) reveals endotherms peaking at 150° and $175^\circ C$, and a strong endothermic peak at $300^\circ C$. These endotherms, commencing at temperatures of ca. $120^\circ C$, substantiated previously reported Russian works which have stated that NaO_2 is unstable at temperatures of about $100^\circ C$, decomposing with the evolution of oxygen [7, 8]. The endotherm, beginning at $270^\circ C$ and peaking at $300^\circ C$, can probably be attributed to the decomposition of sodium superoxide to the peroxide via the reaction:

$$2NaO_2 = Na_2O_2 + O_2 \qquad (1)$$

Vol'nov, however, has reported that this reaction takes place about $278^\circ C$. The higher temperatures recorded here may be attributed to the differences in the program rates employed. In the work at hand, a fairly rapid program rate of 10°/min. was used. This is higher than the rate employed by the Russian investigators[8]. The faster rate might be expected to result in higher transition temperatures because of a greater thermal lag of the sample. Another factor which may have contributed to these higher temperatures was the static atmosphere employed in the DTA runs. Under the conditions utilized here, the oxygen produced in the decomposition of the superoxide may form a layer over the sample, thus retarding further decomposition. Under similar conditions it has been shown that a material which undergoes a reaction whose temperature is a function of O_2 pressure

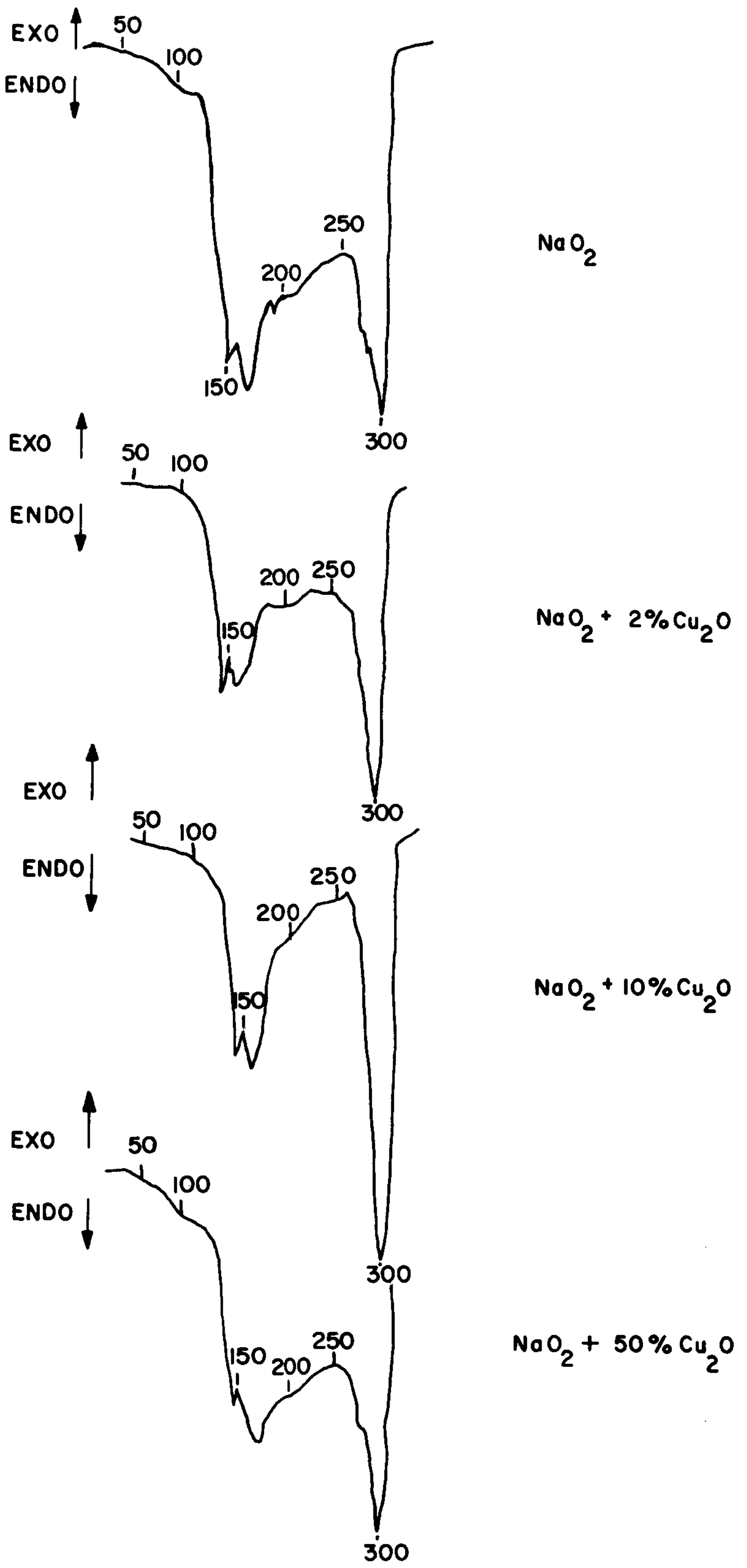


FIGURE 5 DTA THERMOGRAMS FOR SODIUM SUPEROXIDE WITH VARIOUS LEVELS OF COPPER OXIDE CATALYST

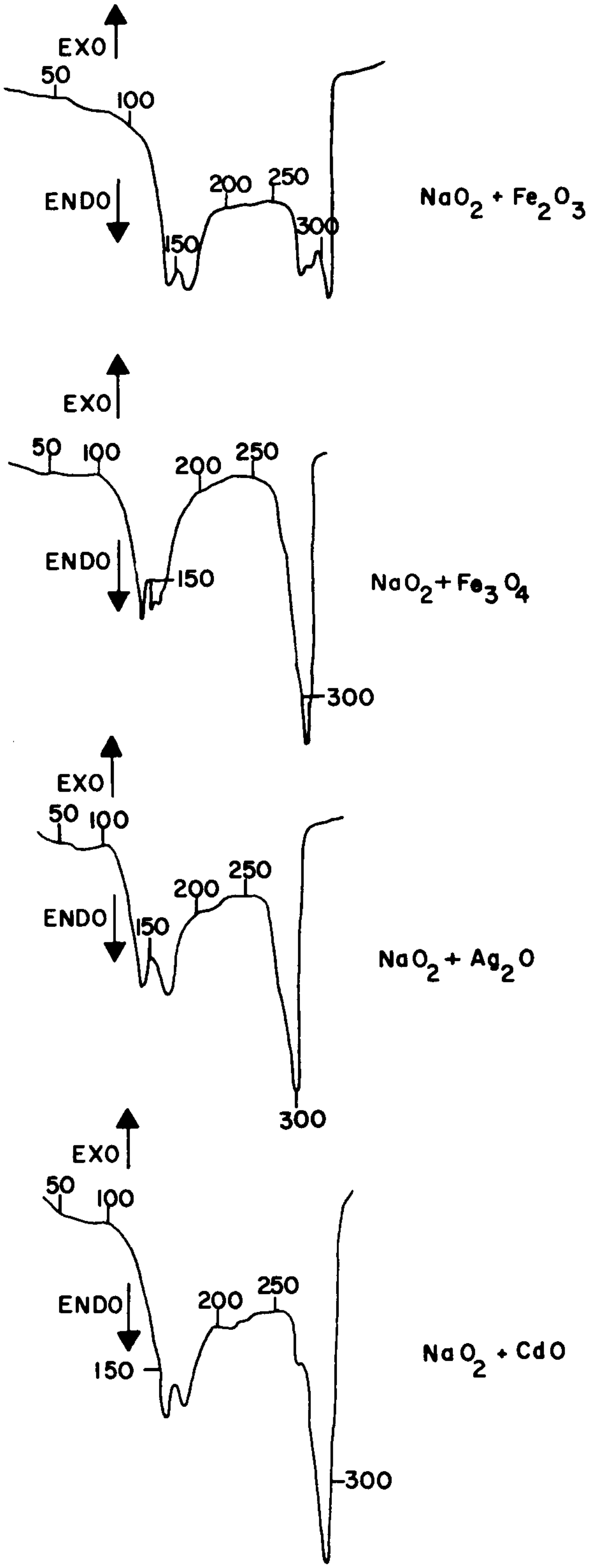


FIGURE 6 DTA THERMOGRAMS FOR SODIUM SUPEROXIDE CONTAINING OXIDES OF IRON, SILVER AND CADMIUM

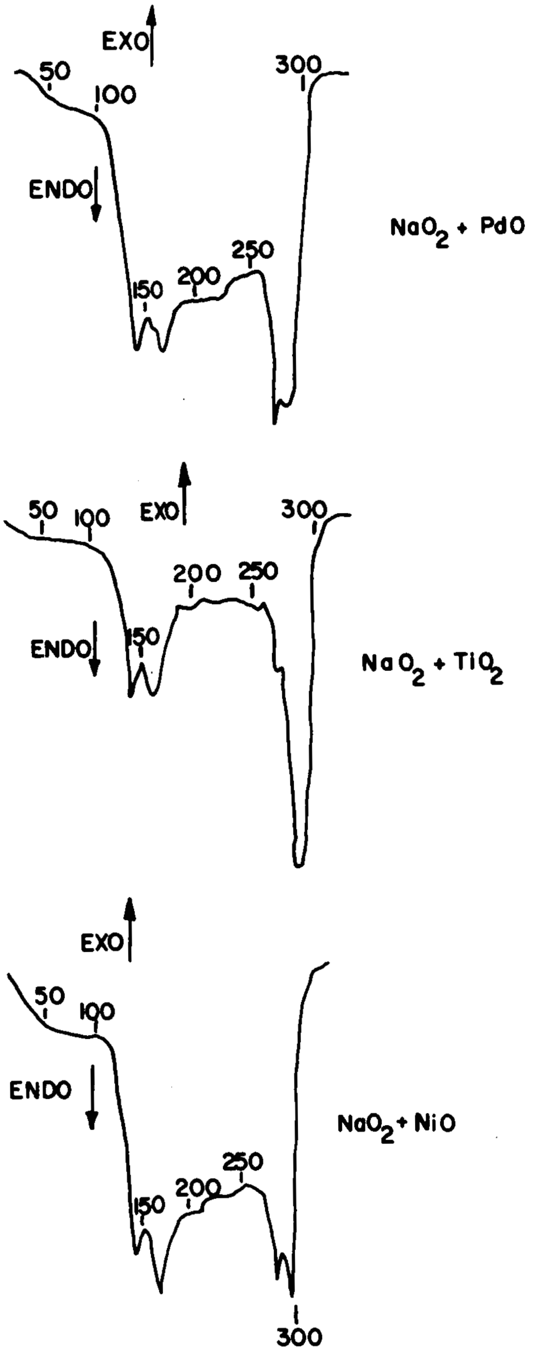


FIGURE 7 DTA THERMOGRAMS FOR SODIUM SUPEROXIDE CONTAINING OXIDES OF PALLADIUM, TITANIUM AND NICKEL

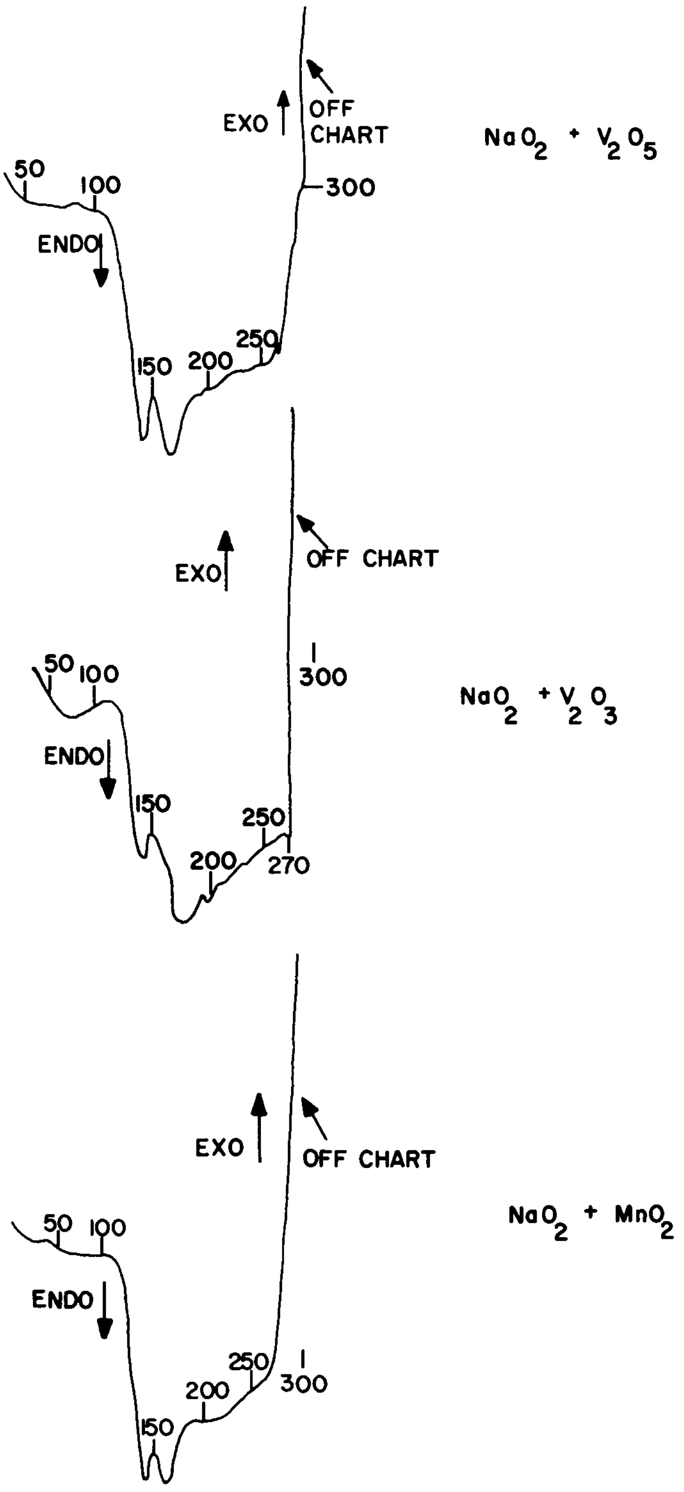
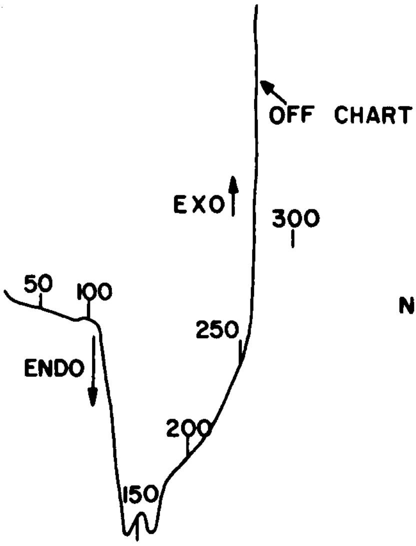
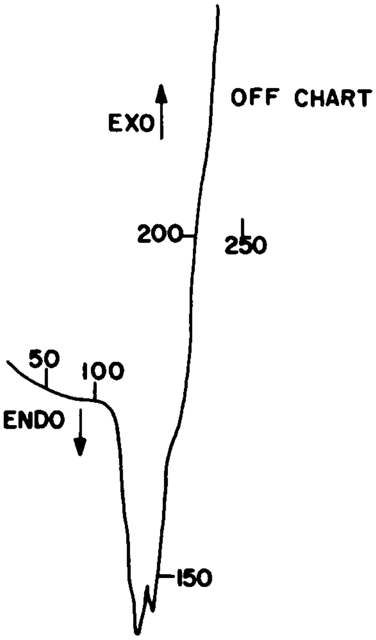


FIGURE 8 DTA THERMOGRAMS FOR SODIUM SUPEROXIDE CONTAINING OXIDES OF VANADIUM AND MANGANESE



NaO_2 + Cu PHTHALOCYANINE I
(POLYMERIC)



NaO_2 + Cu PHTHALOCYANINE II
(POLYMERIC)

FIGURE 9 DTA THERMOGRAMS FOR SODIUM SUPEROXIDE CONTAINING POLYMERIC PHTHALOCYANINES

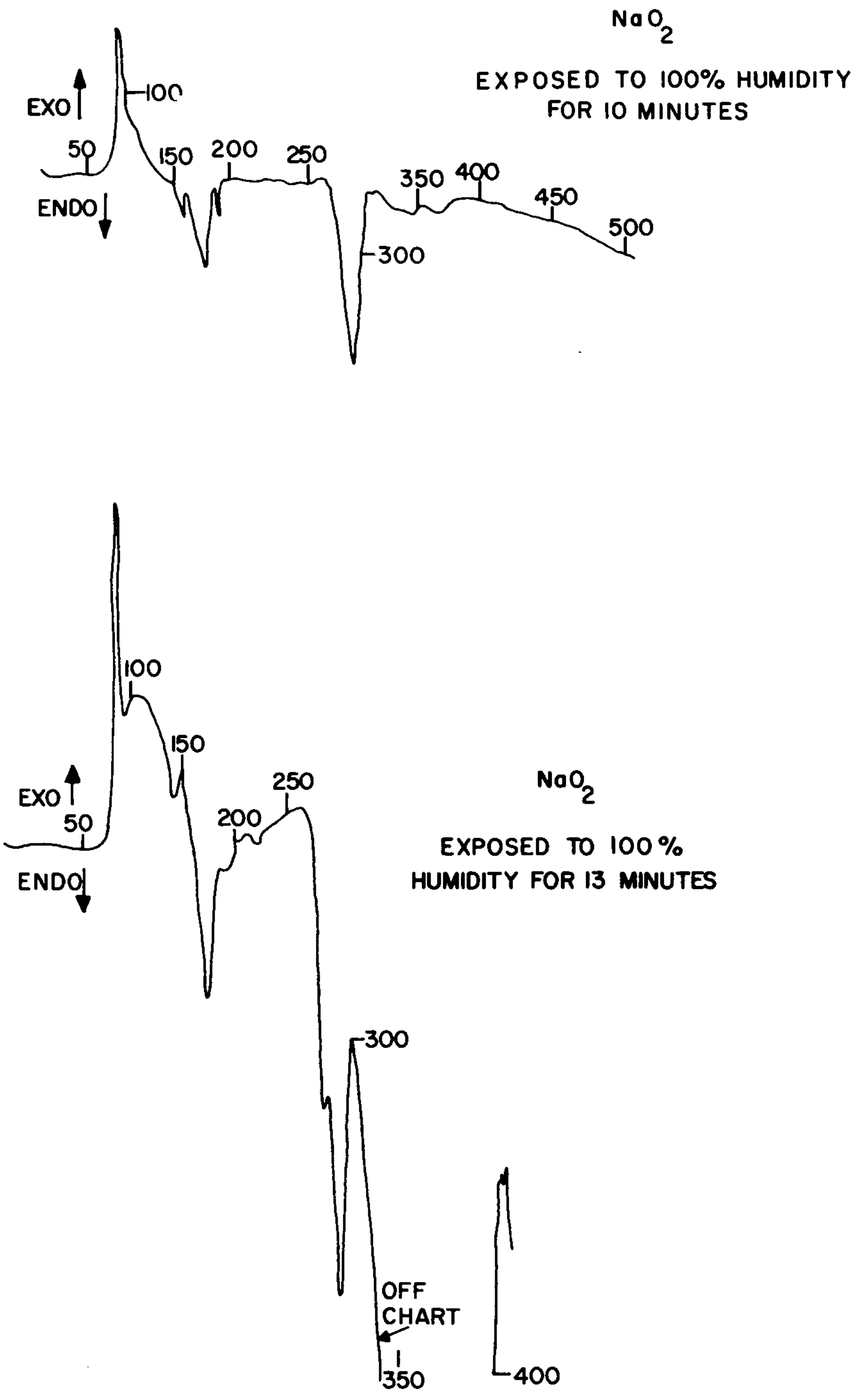


FIGURE 10 DTA THERMOGRAMS OF SODIUM SUPEROXIDE PRECONDITIONED BY EXPOSURE TO 100% HUMIDITY

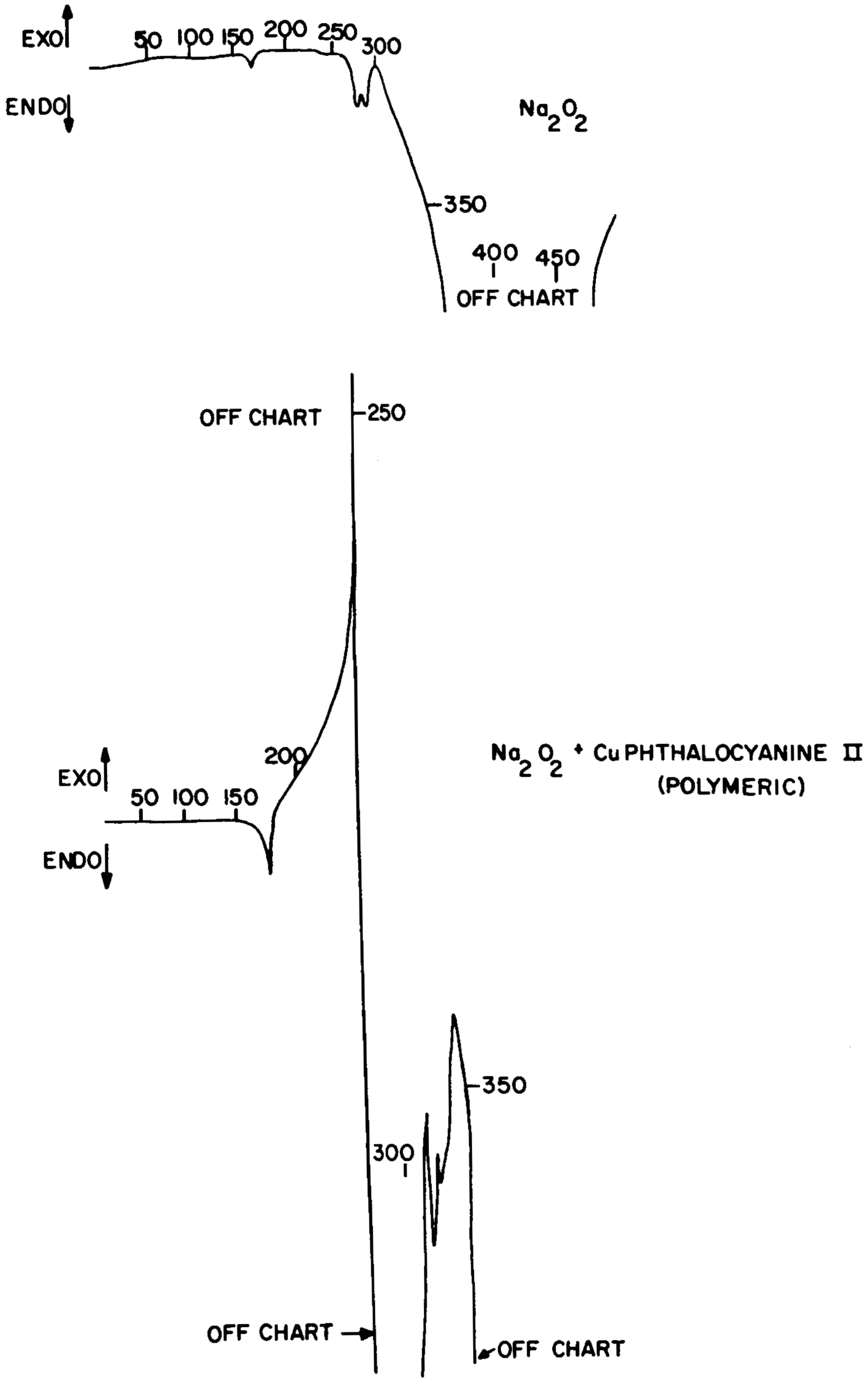


FIGURE 11 DTA THERMOGRAMS FOR PURE SODIUM PEROXIDE AND FOR SODIUM PEROXIDE CONTAINING A POLYMERIC PHTHALOCYANINE

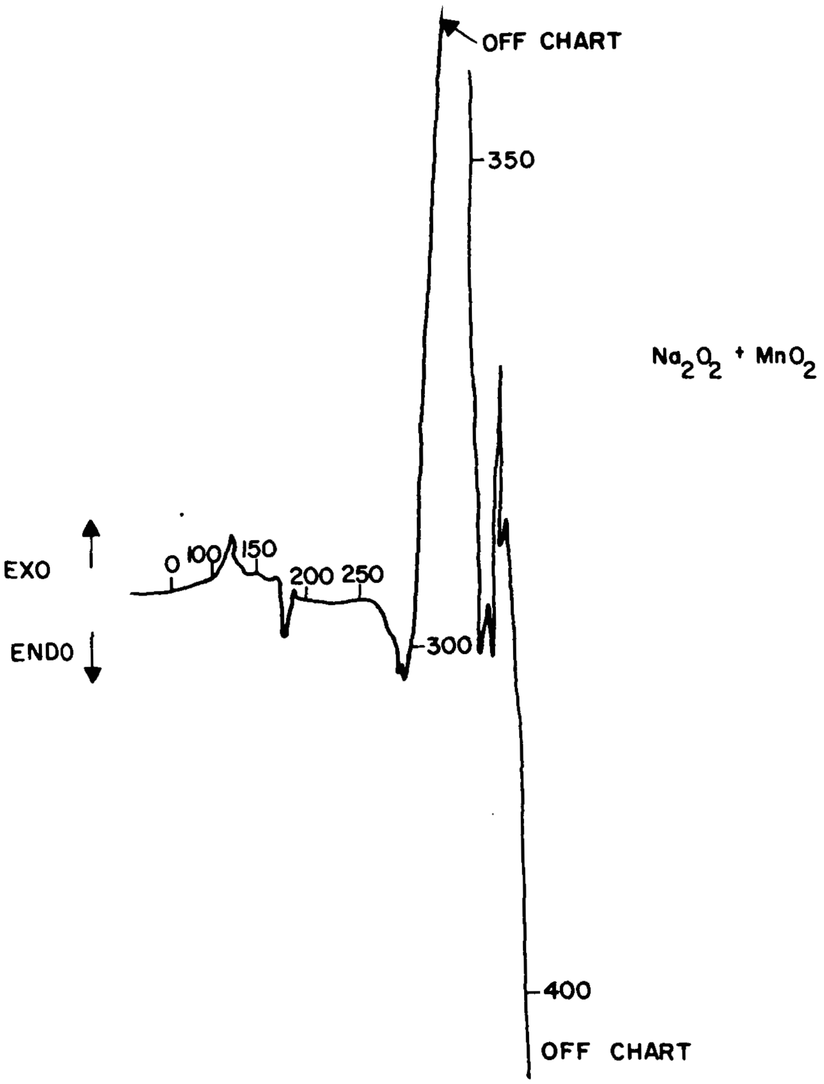


FIGURE 12 DTA THERMOGRAM FOR SODIUM PEROXIDE CONTAINING MANGANESE DIOXIDE CATALYST

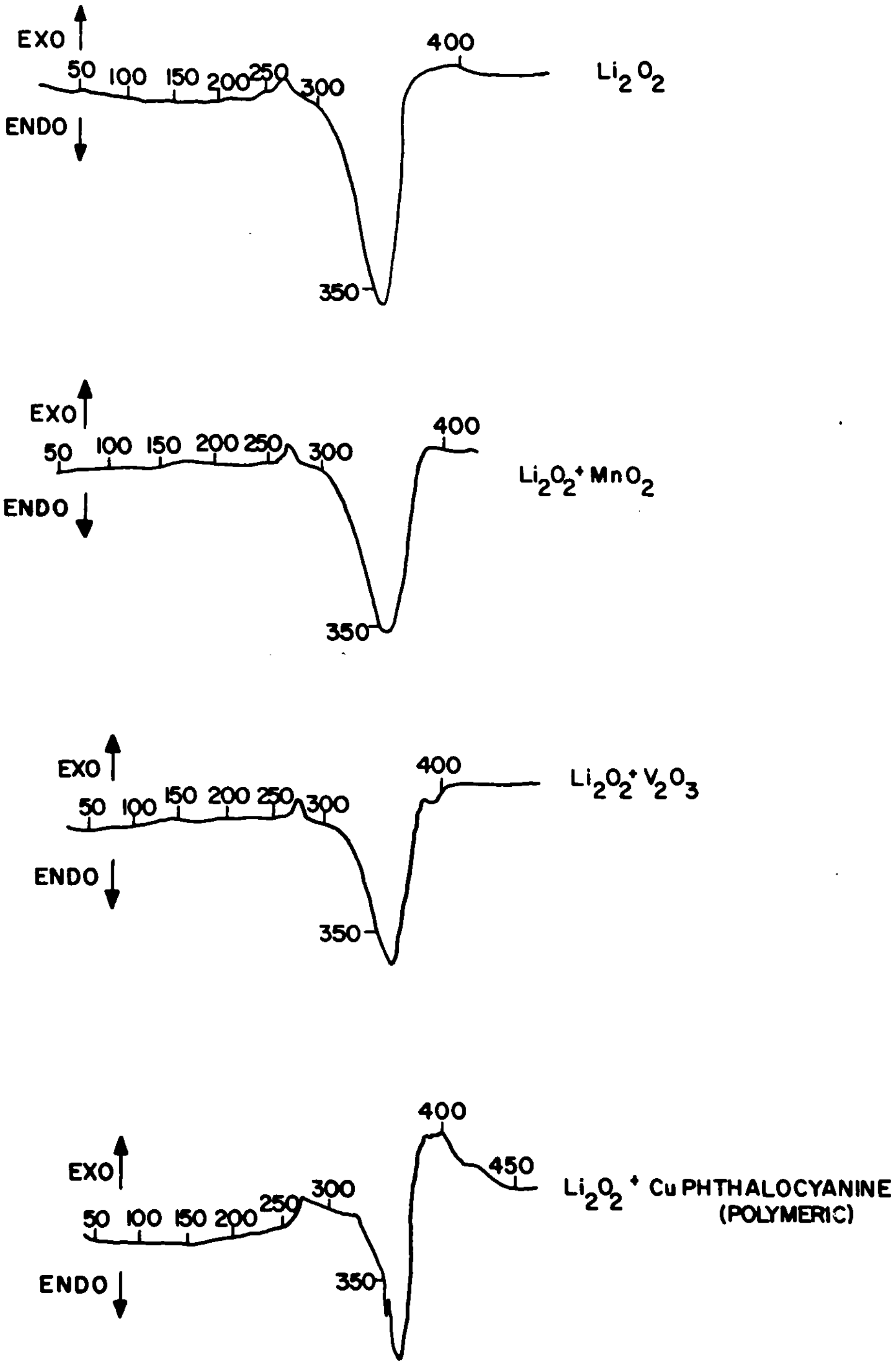


FIGURE 13 DTA THERMOGRAMS FOR PURE LITHIUM PEROXIDE AND FOR LITHIUM PEROXIDE CONTAINING OXIDES OF VANADIUM AND MANGANESE AND A POLYMERIC PHTHALOCYANINE

(or whatever vapor is released by the test material) gives a thermogram in which the shape and temperature of the peaks are noticably affected by experimental variables such as rate of temperature rise, sample packing, grain size, etc.[9]

It is interesting to note that Vol'nov reports that the thermogram of sodium superoxide displays only two endotherms below 500°C: at 145° and 278°C.[8] Our results, however, show three peaks occurring at about 150, 170 and 300°C. These three peaks also appeared on thermograms obtained at an independent laboratory, although the temperatures of occurrence were somewhat lower (See Section C.) A probable explanation is that the samples tested differed in purity. Analytical data have shown that the sodium superoxide tested is about 84% pure.

b. Effects of Metallic Oxide Catalysts

Reference to Figures 6 and 7 reveals that the majority of the catalysts tested caused no major changes in the DTA thermogram of sodium superoxide. Slight differences in the proportion and relative shapes of the 150° and 170° peaks can be noted in a few cases (Fe_3O_4, CdO, Cu_2O (2%)), but no shift in the temperatures of the transitions were noted. Exceptions to this behavior are manganese dioxide, vanadium(V)oxide, vanadium(III)oxide and the polymeric pythalocyanines. Superoxide samples containing these catalysts did not display the usual endotherm at 300°C. Rather, large exothermic peaks were observed at this temperature (Figure 8 and 9). Samples catalyzed by the polymeric copper phthalocyanines showed this strong exotherm, beginning as low as 200°C. On the basis of this activity, these catalysts were selected for further investigation. The results of these further studies are given in a later section.

c. Effect of Preconditioning of NaO_2

The DTA thermograms obtained for samples of NaO_2, which were first exposed to a 100% humid atmosphere, are given in Figure 10. Immediately obvious is the sharp exothermic peak at 80°C. A similar exothermic effect in this temperature range has been observed with a number of peroxy hydrates ($M_2O_2 \cdot H_2O_2$) and has been attributed to the dissociation of the crystallized hydrogen peroxide [10, 11] The occurrence of this peak indicates the probability of a reaction of the following type taking place upon water absorption:

$$2NaO_2 + XH_2O = Na_2O_2.XH_2O_2 \qquad (2)$$

In this regard, it should be noted that the decomposition temperature of sodium peroxide dihydroperoxiate has been reported as 157°C [12], and indeed an endothermic peak occurs in this temperature range on the thermograms.

Of particular interest is the peak beginning at ca. 265°C, for it is at this temperature that sodium superoxide converts to the peroxide. The thermogram of pure NaO_2 (Figure 5) shows this peak at 300°C while with the preconditioned samples of superoxide, a shift to lower temperatures is observed. Preconditioning by exposure to high humidities, therefore, may lower the decomposition temperature of sodium superoxide slightly.

In studying the effects of preconditioning on the thermal stability, the time of exposure, the relative humidity, and the exposed surface area must be carefully noted. If the sample is exposed to the atmosphere for too long, a whitening attributable to the formation of peroxides, hydroxides, or other decomposition products is observed. Using 100% humid atmosphere and 80 mesh NaO_2, the time period for whitening to occur was found to be about 12 minutes when a watch glass containing about 0.25 grams was placed in the humid chamber. With shorter periods of exposure, a caking of the sample was observed but no whitening occurred. Of course with atmospheres containing less than 100% humidity longer exposure periods would be tolerable.

The effect of exposure time on the stability of NaO_2 is clearly seen in Figure 10. The sample exposed for 13 minutes was noticeably whitened and gave a very strong endothermic trough at temperatures greater than 300°C corresponding to complete disintegration of the material. The sample exposed for only 10 minutes, however, displayed no activity at these temperatures.

d. Pure Na_2O_2 and Li_2O_2

Although the major part of this effort was concentrated on the thermal properties of sodium superoxide, some work was devoted to the decomposition of sodium and lithium peroxides. The DTA curve for the pure Na_2O_2 compound is given in Figure 11. The thermogram shows a small endotherm at ca. 165° which may be traced to the presence of small amounts of $Na_2O_2 \cdot 2H_2O_2$ (decomposition point 157°C).[12] The curve indicates that the peroxide begins to decompose above 310°C. Above 350° the endotherm was uncontrollable, going completely off the chart. It has been previously reported that Na_2O_2 decomposes with the liberation of oxygen between 311° and 400°C.[12]

The effects of a polymeric copper phthalocyanine and manganese dioxide on the stability of sodium peroxide can be seen in Figures 11 and 12. The Na_2O_2 - Cu phthalocyanine thermogram shows the familiar endotherm at ca. 165°C, and then displays a strong, sharp exotherm followed immediately by the endothermic decomposition. This mixture, when heated suddenly to 250°C, detonated. The peroxide appeared to oxidize the organic portion of the phthalocyanine, leaving a copper salt residue.

The Na_2O_2-MnO_2 mixture also showed increased activity. The curve displays an exotherm at ca. 110°C which is similar to peaks observed for the decomposition of $M_2O_2.XH_2O_2$. This catalyst also caused a very strong exothermic peak commencing at 300°C. An interesting observation was that the residue from this reaction was bright blue. A precise explanation for this phenomenon is not immediately available. The color, however, may be due to the formation of compounds of general type $MnO_2.XH_2O_2$. Another possible explanation may be the formation of $MnO_4^{=}$ ion or even a peroxide of the type MnO_4. The blue material was unstable, decomposing upon contact with air to form a gas and a white residue.

The DTA thermograms for pure Li_2O_2 and several catalyzed samples are given in Figure 13. The relatively simple curves display a slight exothermic bump at ca. 260°C which has been ascribed by several authors[13,14,15] to a reversible polymorphous phase change. The endotherm corresponding to the decomposition to the oxide begins slightly above 300°C. It is seen that the catalysts employed (MnO_2, V_2O_3, CuPh) have little effect on the thermograms. Only the phthalocyanine catalyst produced an additional peak, a slight exotherm at ca. 380°C.

Because the decomposition temperature of lithium peroxide was significantly high ($>$ 300°C), and since the catalysts investigated did not effect a decrease in this temperature, isothermal kinetic studies were not conducted on this material.

2.1.8. Results of Thermogravimetric Studies (TGA)

a. Calibration of Thermobalance

Before conducting the TGA studies on the pertinent superoxide compounds, the thermobalance, previously described, was calibrated by performing a blank run with an empty sample pan. Figure 14 shows the thermal characteristics of the balance based on data obtained from this analysis.

The accuracy of the recorded weight losses was then checked by analyzing a sample of copper sulfate pentahydrate (Figure 15 shows the TGA curve resulting from this analysis). The recorded weight loss of 27.8% is in close agreement with the theoretical value of 28.8% which corresponds to the loss of four molecules of water. This is in accord with previous experimental work which has shown that the first four water molecules of $CuSO_4 \cdot 5H_2O$ are lost relatively easily while the fifth, being coordinated to the anion instead of the metal, is lost only with difficulty at higher temperatures (300°C)[16].

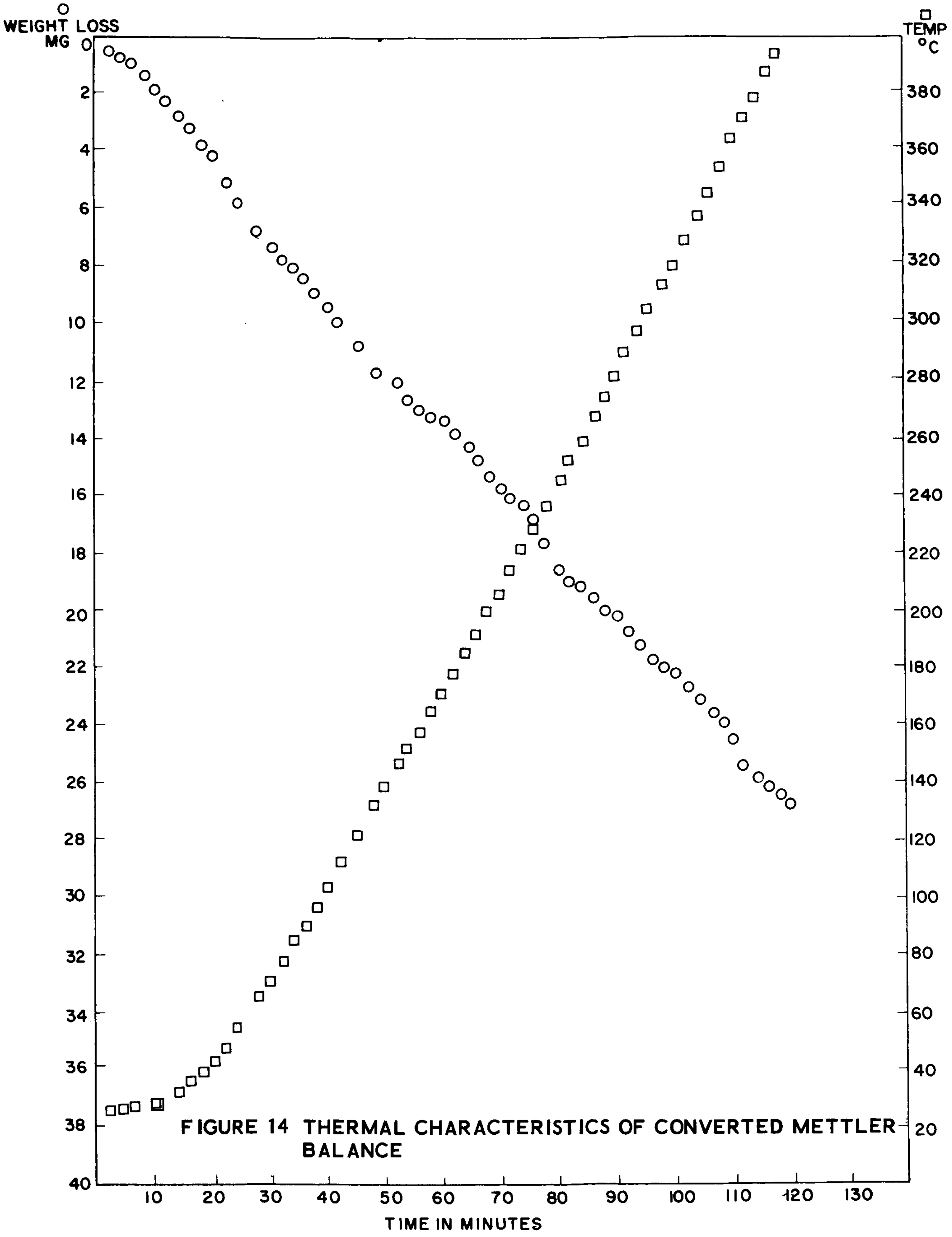


FIGURE 14 THERMAL CHARACTERISTICS OF CONVERTED METTLER BALANCE

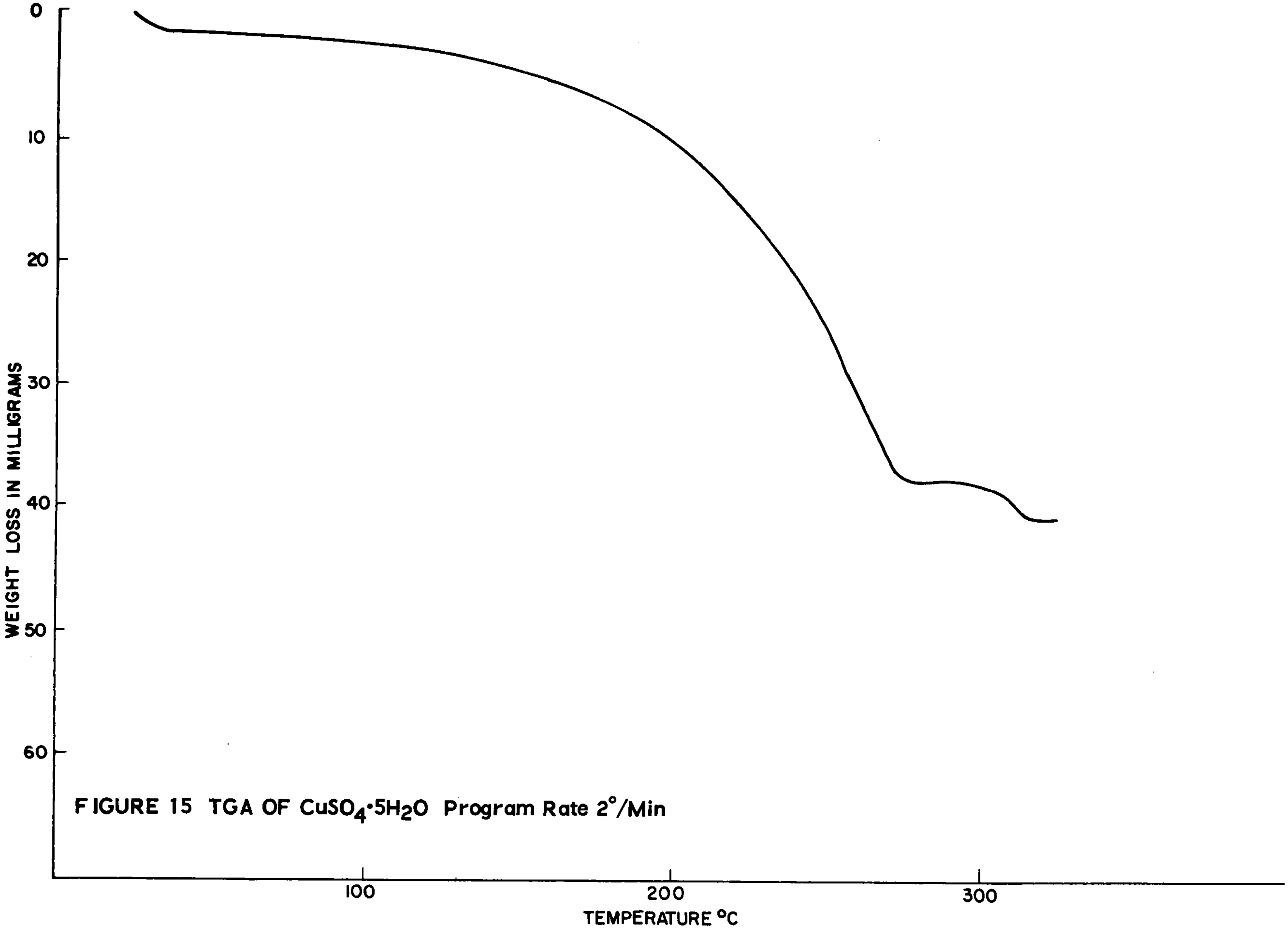


FIGURE 15 TGA OF $CuSO_4 \cdot 5H_2O$ Program Rate 2°/Min

b. Analysis of NaO_2

The TGA thermogram for sodium superoxide is shown in Figure 16. The curve shows a small initial weight loss beginning about 120°C, with the principal decrease in weight beginning about 250°C and becoming quite rapid at temperatures of 290-300°C.

A similar curve was obtained with a catalyzed sample of sodium superoxide containing vanadium(V) and aluminum oxides (Figure 17). In the presence of these catalysts, however, the weight loss became very rapid at a lower temperature ($>$ 210°C).

Because of the gradual onset of weight loss, it was difficult to determine the initial temperature at which the samples started to decompose. On this basis and because TGA work was so time consuming, it was decided to utilize the DTA curves to select the temperatures at which kinetic studies were to be conducted. No further TGA work, therefore, was carried out in this research. Additional weight loss curves, however, were obtained by the Mettler laboratories and are discussed below.

2.1.9 Results of Simultaneous DTA - TGA and DTG

Differential thermal analysis, thermogravimetric and differential thermogravimetric curves were obtained simultaneously on several selected samples at the Mettler Company's laboratories. The analyses were performed utilizing the Mettler recording vacuum thermoanalyzer employing a program rate of 4° per minute. Aluminum oxide was used as reference material and the atmosphere was dry air, at a flow rate of 5.7 liters per hour.

The four samples which were selected for study were pure NaO_2, NaO_2 containing 1% cuprous oxide catalyst, pure lithium peroxide, and lithium peroxide containing 1% cuprous oxide catalyst. Figures 18 through 21 represent the thermograms reported by the Mettler Company Laboratories.

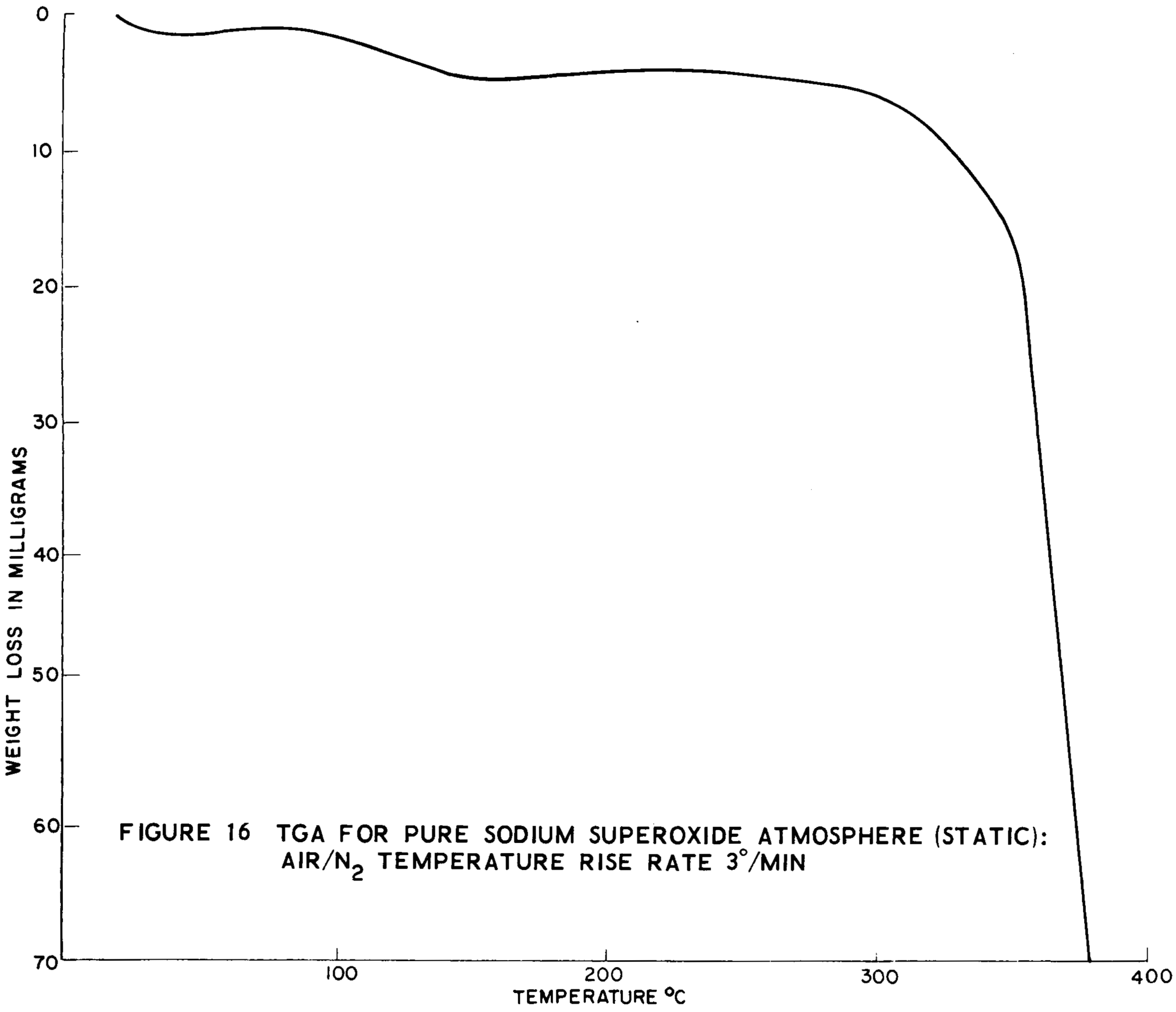


FIGURE 16 TGA FOR PURE SODIUM SUPEROXIDE ATMOSPHERE (STATIC): AIR/N_2 TEMPERATURE RISE RATE 3°/MIN

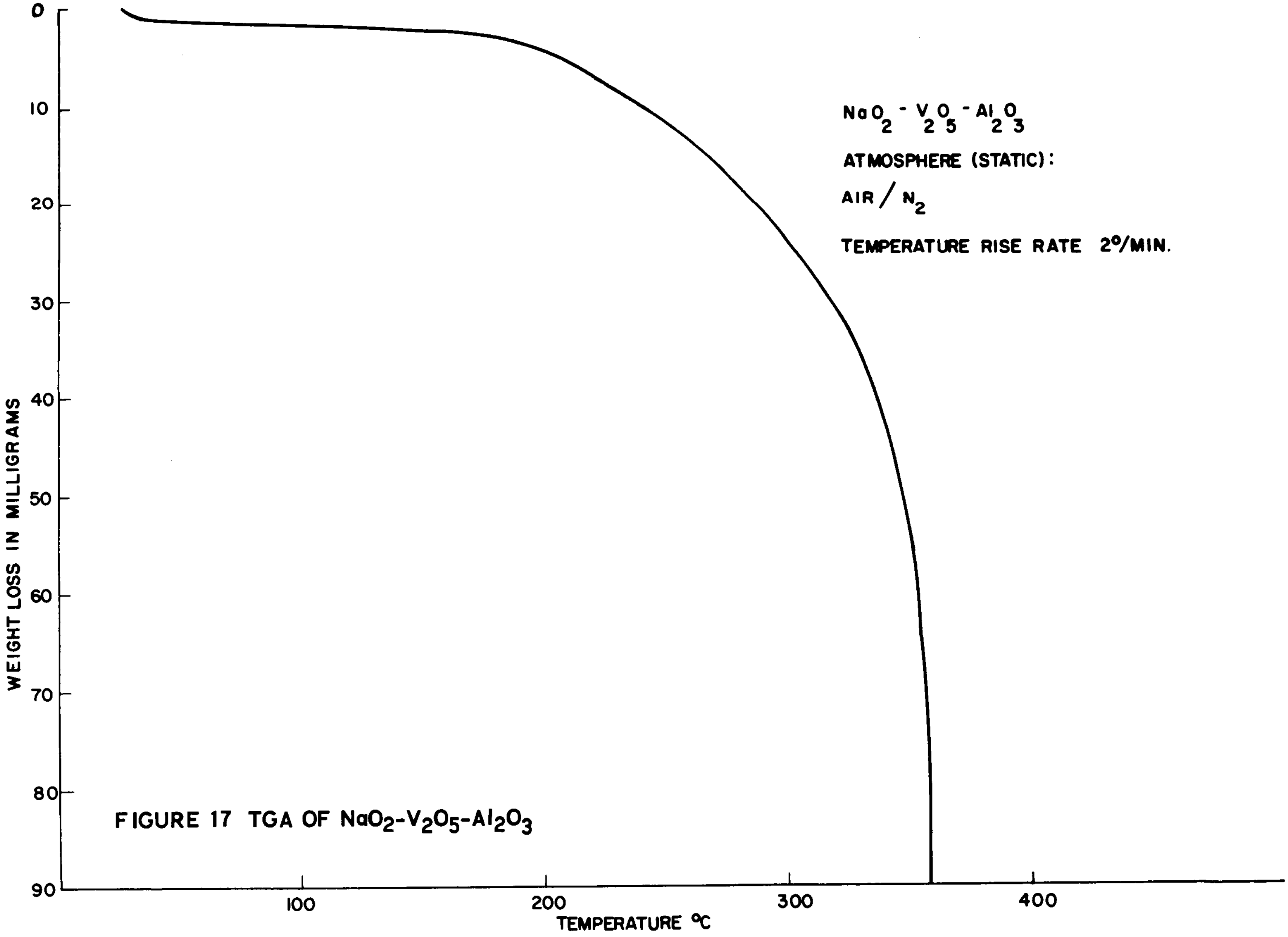
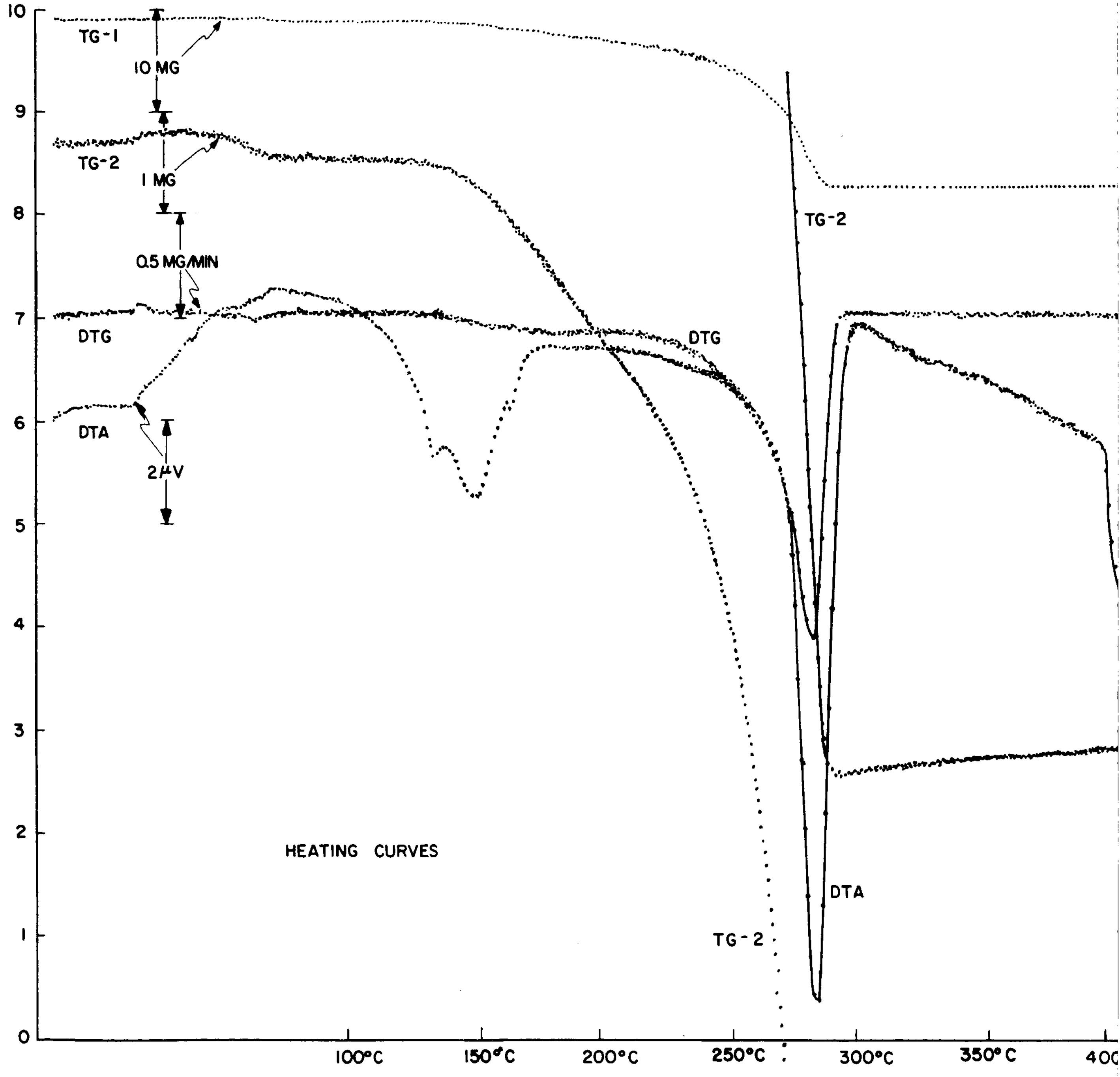


FIGURE 17 TGA OF NaO_2-V_2O_5-Al_2O_3


10
9
8
7
6
5
4
3
2
1
0
TG-1
10 MG
TG-2
1 MG
0.5 MG/MIN
DTG
DTA
2 μV
HEATING CURVES
TG-2
DTG
DTA
TG - 2
100°C
150°C
200°C
250°C
300°C
350°C
40

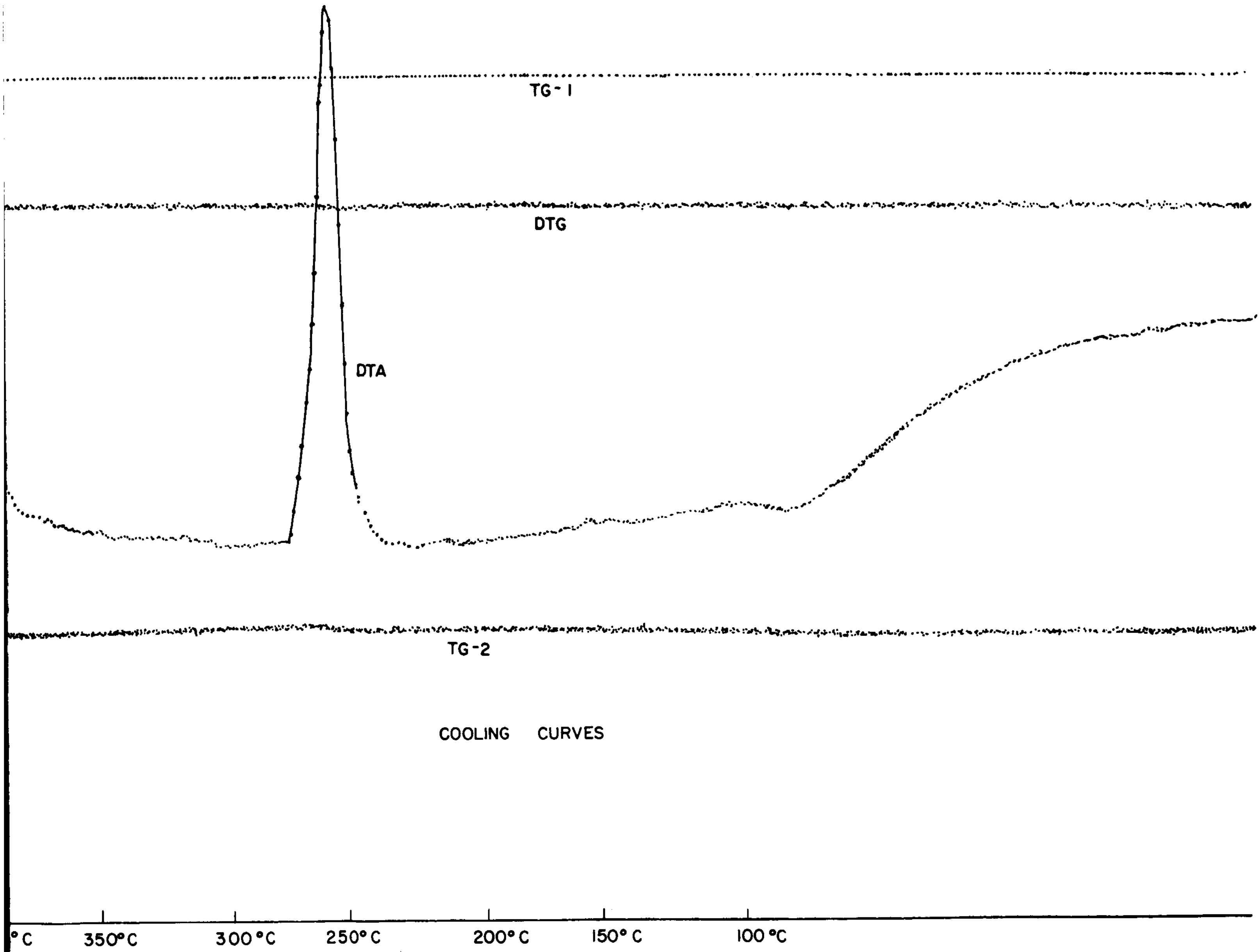
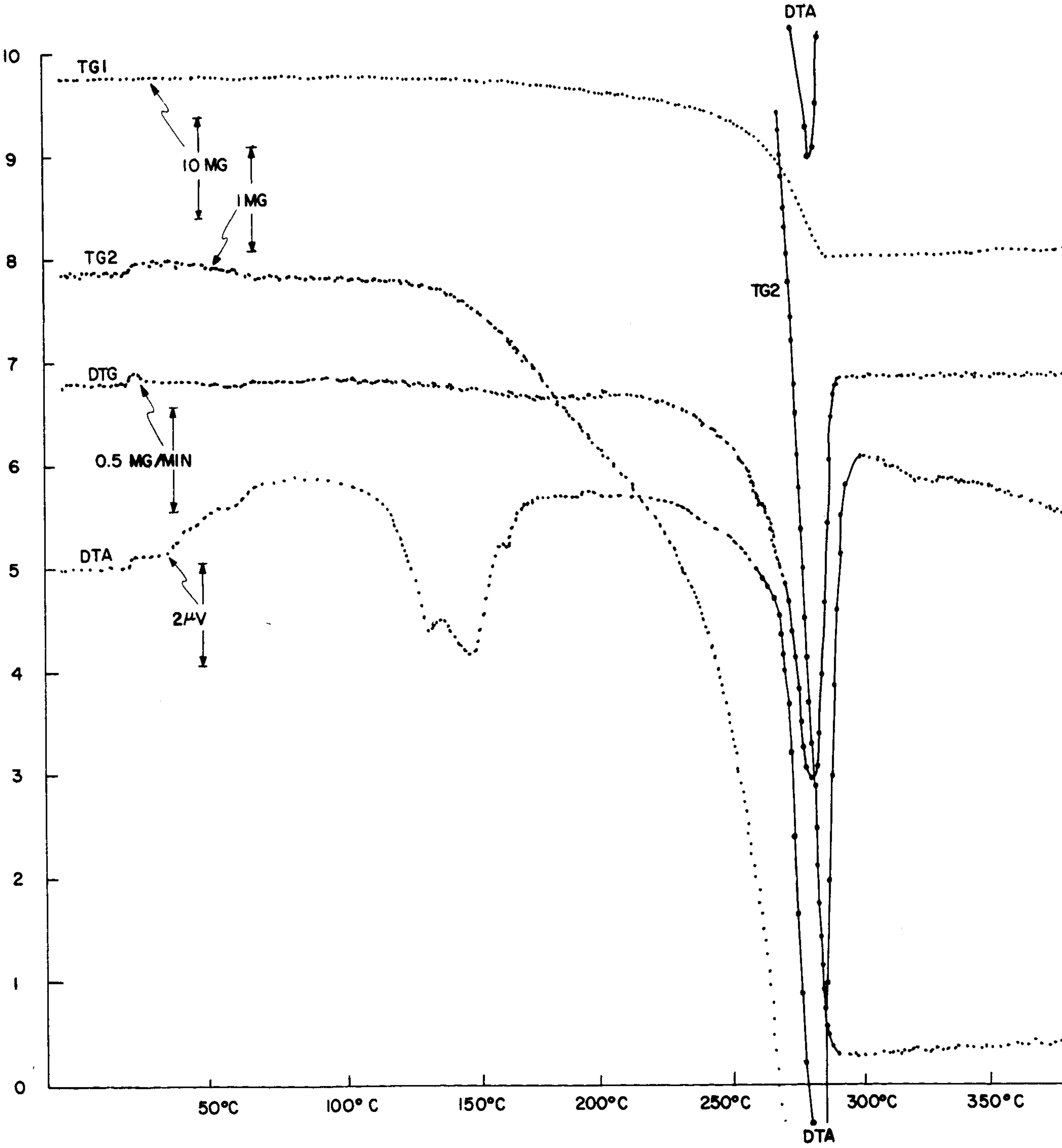


FIGURE 18 SIMULTANEOUS DTA-TGA-DTG FOR NaO_2



DTA
10
TG1
9
10 MG
1 MG
8
TG2
TG2
7
DTG
0.5 MG/MIN
6
DTA
5
2μV
4
3
2
1
0
50°C
100° C
150°C
200°C
250°C
300°C
350°C
DTA

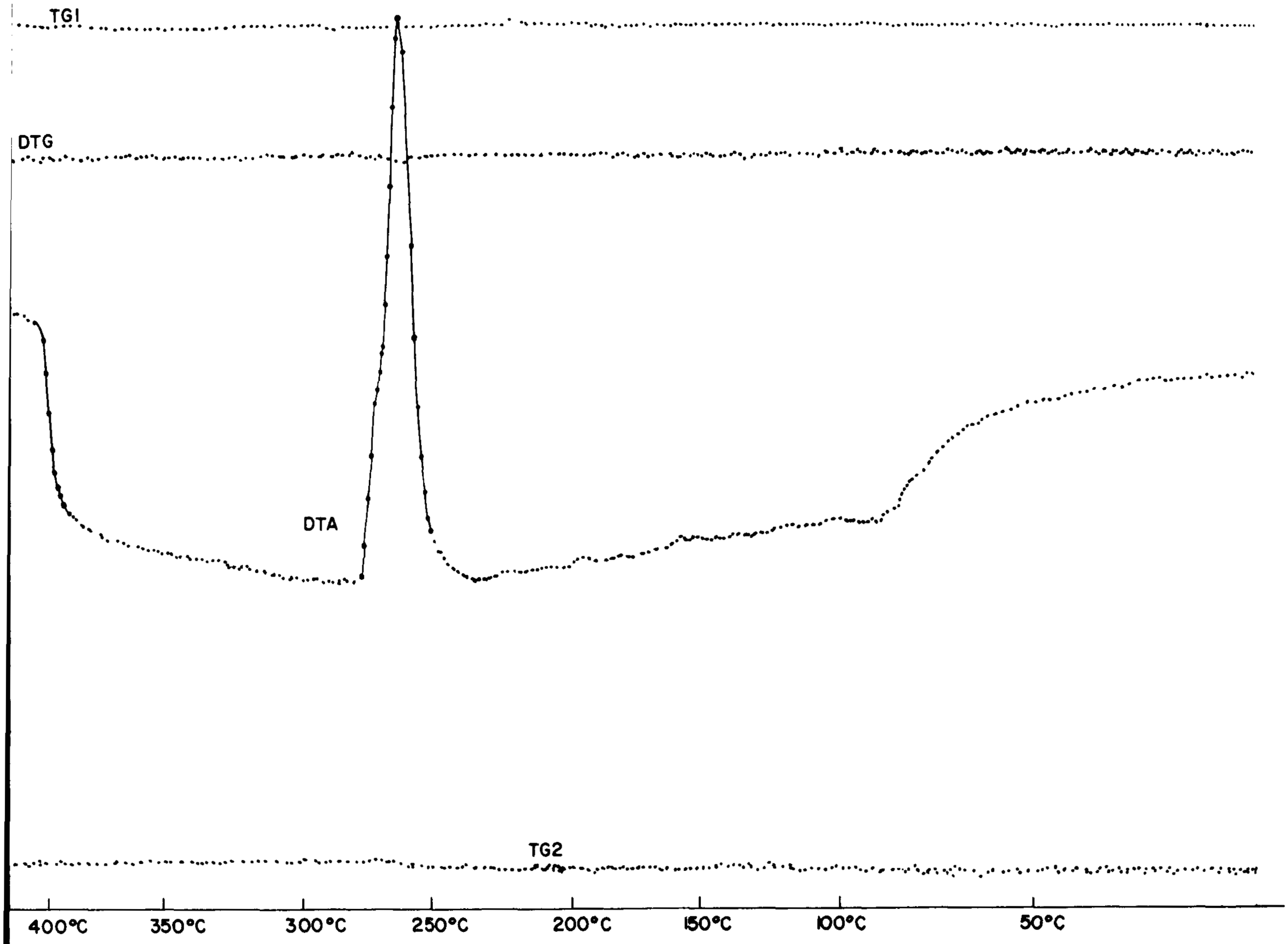
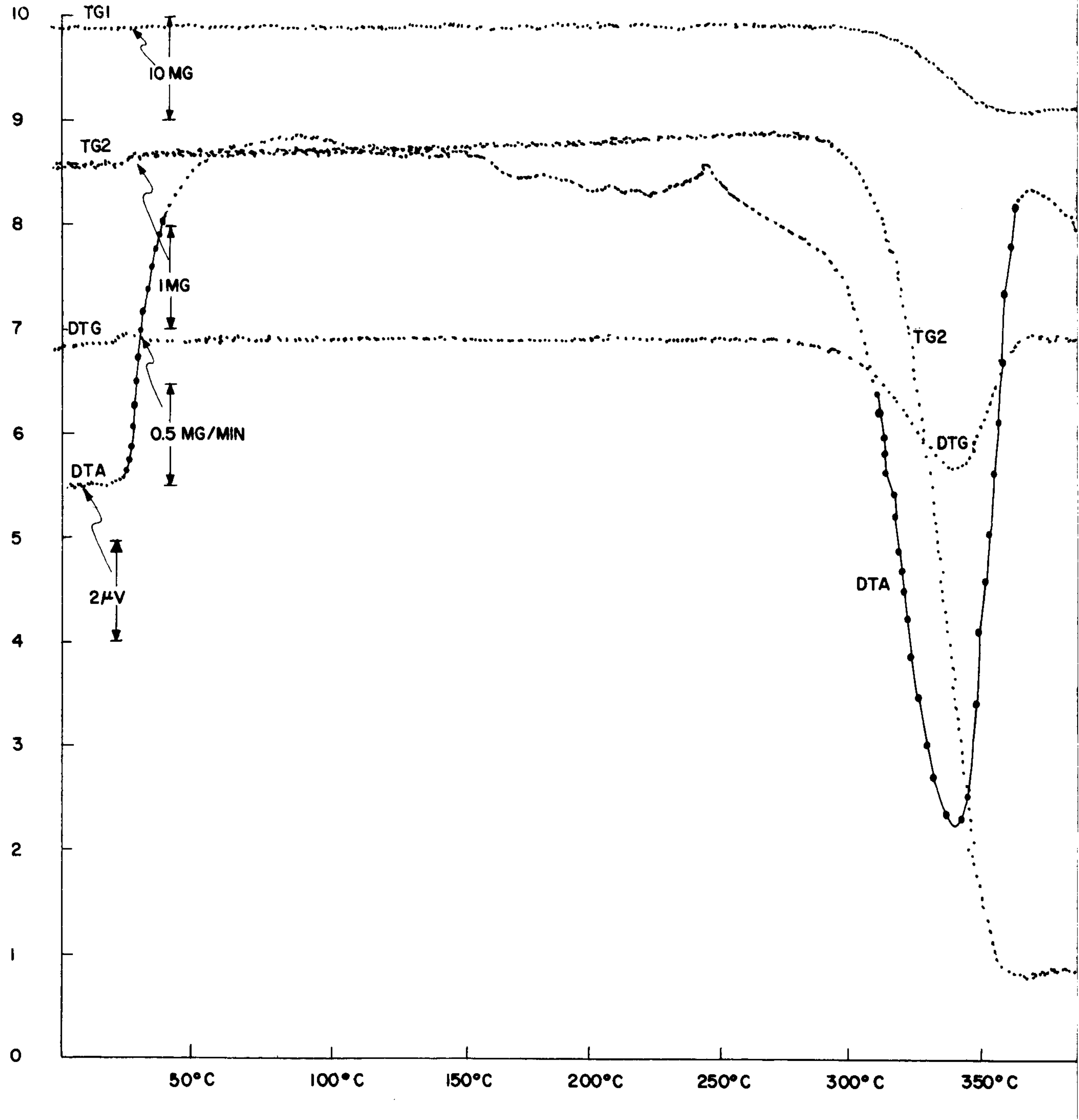


FIGURE 19 SIMULTANEOUS DTA-TGA-DTG FOR $NaO_2 + 1\% \ Cu_2O$


10
9
8
7
6
5
4
3
2
1
0
TG1
10 MG
TG2
1MG
DTG
0.5 MG/MIN
DTA
2μV
TG2
DTG
DTA
50°C
100°C
150°C
200°C
250°C
300°C
350°C

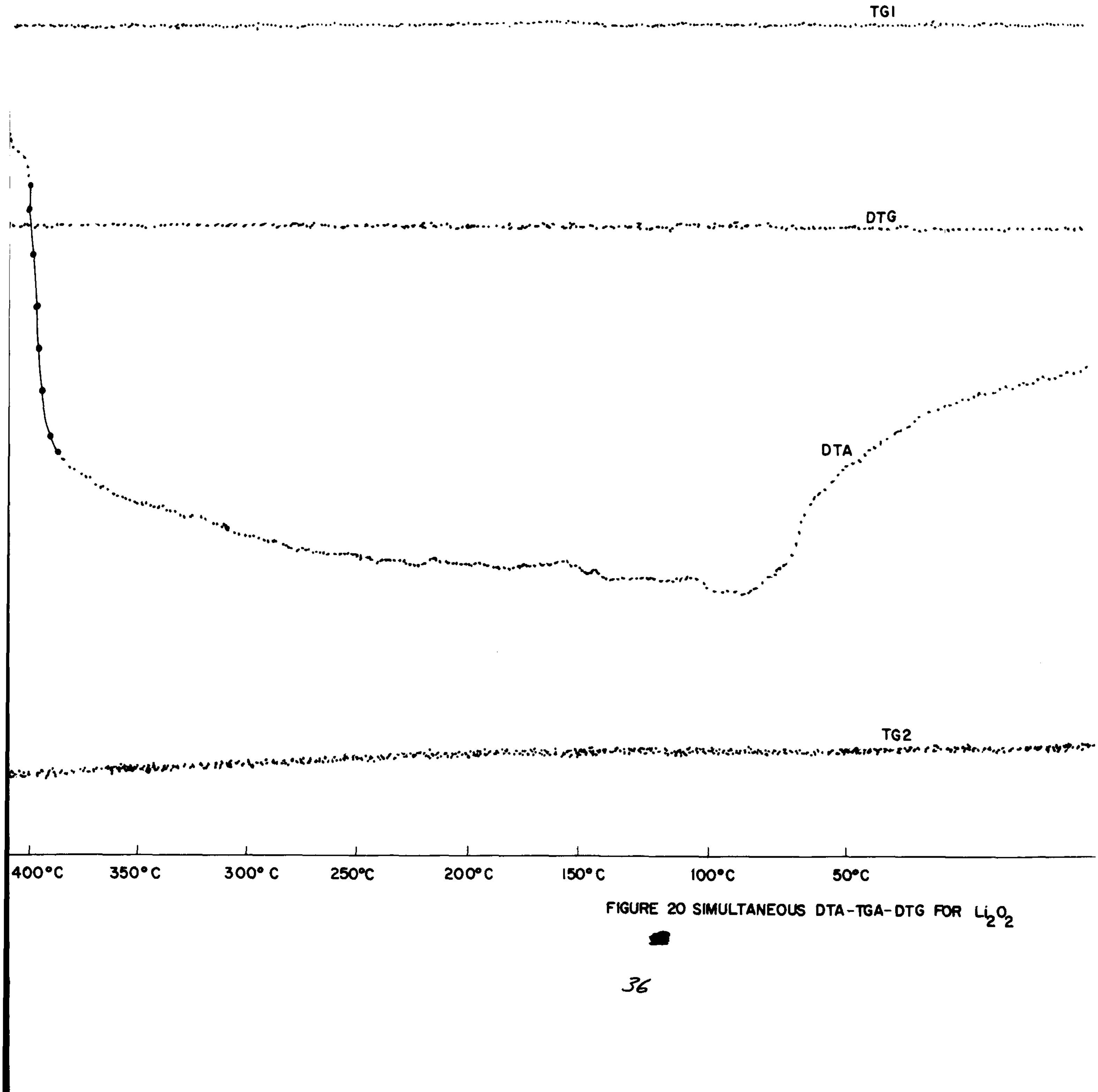
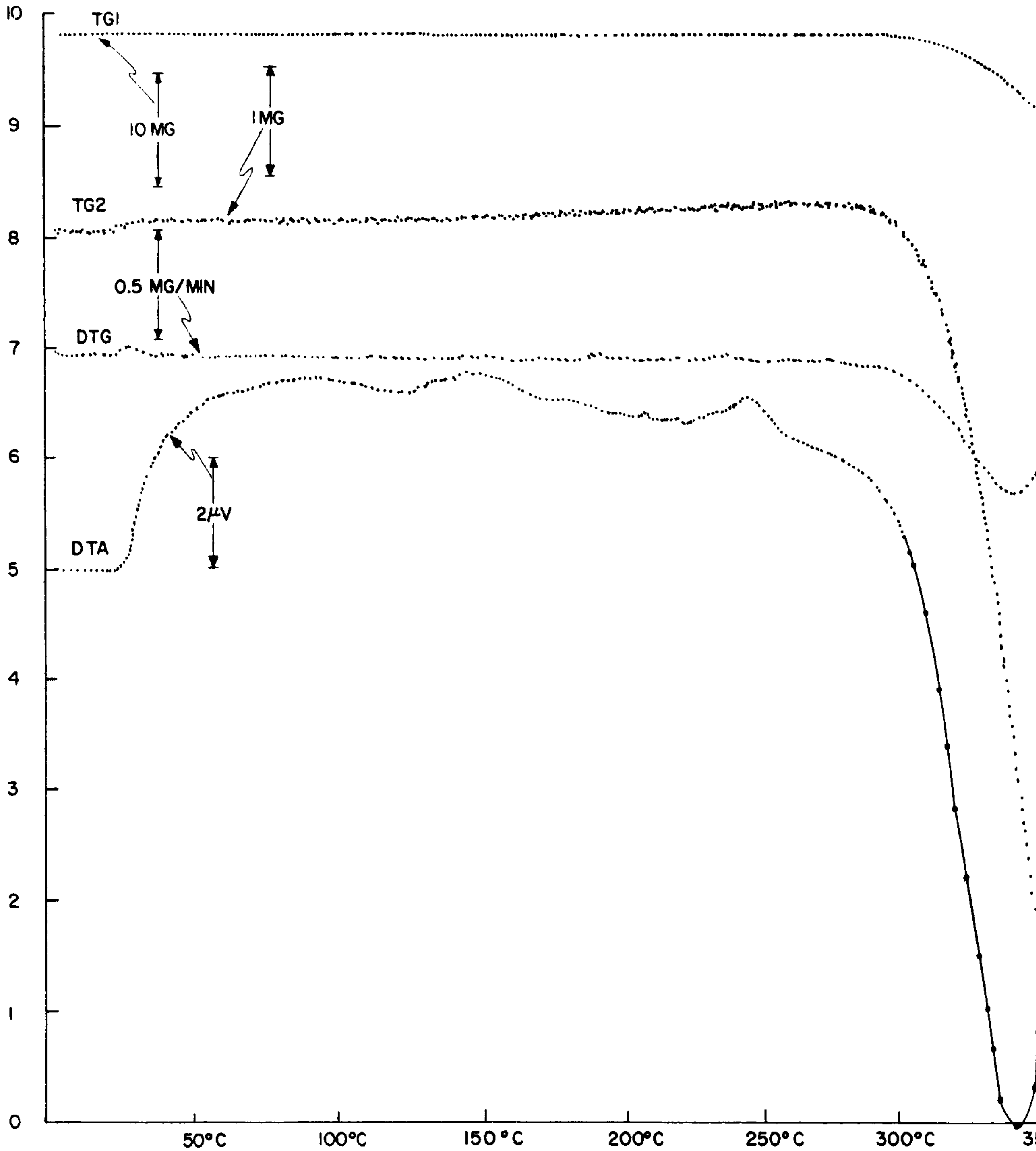


FIGURE 20 SIMULTANEOUS DTA-TGA-DTG FOR Li_2O_2



TG1
TG2
DTG
DTA
10 MG
1 MG
0.5 MG/MIN
2μV
10
9
8
7
6
5
4
3
2
1
0
50°C
100°C
150°C
200°C
250°C
300°C

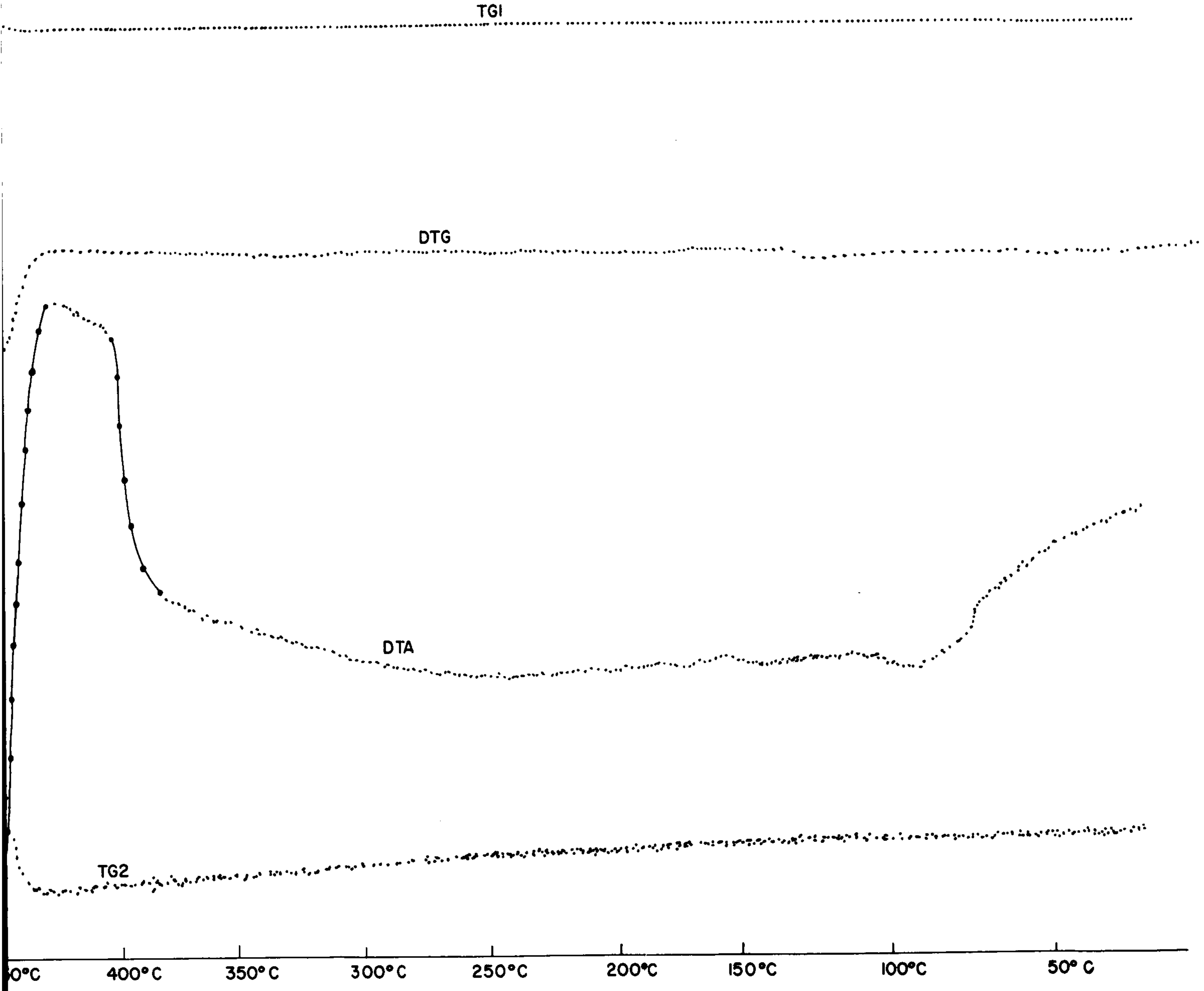


FIGURE 21 SIMULTANEOUS DTA - TGA - DTG FOR Li_2O_2 + 1% Cu_2O

a. NaO_2 and NaO_2 - Cu_2O (1%)

The DTA thermogram for NaO_2(Figure 18) shows three principal endothermic peaks at ca. 135°, 150°, and 285°C. At the same time, the weight loss curve (TG-1) exhibits only a slight decrease in weight at temperatures lower than 200°C, with the principal break in the curve occurring in the 250°C range. The expanded thermogravimetric curve (TG-2 = 10xTG-1) shows this break more clearly. From these curves it may be concluded that the principal decomposition of sodium superoxide involving the production of oxygen (weight loss) does not occur at a meaningful rate until temperatures near 250°C are attained.

The curves for the sodium superoxide-cuprous oxide sample (Figure 19) display identical peaks on the DTA curve and a similar break on the TGA thermogram. It is noted, however, that the break in the TGA curve for the catalyzed sample is a little sharper than that of the pure sample. Since the DTA peaks for the copper containing sample coincide exactly with those of pure sodium superoxide, it would seem that this catalyst has no effect on the decomposition temperature.

Examination of the DTG curves for the two samples reveal sharp peaks in both cases at ca. 285°C. With the pure sample, the peak length represents a maximum weight loss rate of 15.5 mg/min, while with the catalyzed material the rate indicated is 19.0 mg/min. It appears, therefore, that the addition of cuprous oxide may cause a slight increase in the rate of decomposition even though the decomposition temperature does not appear to be affected.

These simultaneous analyses were carried out to a temperature of 400°C, at which time the furnace was turned off and the cooling curves were traced from 400° to room temperature. It is interesting to note that the DTA cooling curve for NaO_2 displays a strong exotherm at about 260°C while no comparable weight change is recorded at this temperature on the TGA cooling curve (TG-1 or TG-2). This exothermic peak probably represents the reverse of an endothermic process which appeared at 285°C on the heating curve. Its presence, therefore, indicates the occurrence of a reversible physical transition. It is remembered, however, that the endotherm at 285°C on the heating curve has been attributed to the decomposition of sodium superoxide to sodium peroxide and oxygen (an irreversible chemical change). The appearance of the exotherm on cooling, therefore, indicates that either the product formed in the decomposition of the superoxide (sodium peroxide), or the residual sodium superoxide must undergo a reversible phase transition in the 250-285°C temperature range. In this regard, it should be pointed out that the compound $Na_2O_2.H_2O$ has been reported to melt at 285°C. Trace amounts of water present in the original superoxide sample could account for the formation of this compound and hence the appearance of the exotherm on cooling (via crystallization). The DTA curve for Na_2O_2 shows only a minor endotherm at 285°C.

b. Li_2O_2

The thermograms obtained for Li_2O_2 and Li_2O_2/Cu_2O systems were much simpler than those obtained with the superoxide. The DTA curve for the pure Li_2O_2(Figure 20) shows a single endotherm beginning at ca. 300°C, which corresponds to the decomposition to lithium oxide.

$$Li_2O_2 \longrightarrow Li_2O + 1/2O_2 \qquad (3)$$

The thermogravimetric curves (TG-1 and TG-2) show the weight loss occurring simultaneously at this temperature. From the length of the DTG peak, occurring at 340°C, a maximum weight loss rate of 6.0 mg/min was calculated.

The small exothermic bump occurring about 245°C has been noted by other investigators and its origin is still questionable.

It is seen that no weight loss occurs at this point and that the break is not reversible on the cooling. The source of the exotherm then, must be some irreversible, physical transition. Markowitz has suggested the peak may represent the crystallization of small amounts of amorphous lithium peroxide,[17] while other investigators have suggested an irreversible α-β crystallographic transition[13]. The question, however, has not yet been resolved.

Simultaneous DTA-TGA analysis on the Li_2O_2-Cu_2O system yielded thermograms identical to those obtained with pure lithium peroxide. No differences could be detected in the temperature or rate of decomposition (Figure 21).

2.2 ISOTHERMAL KINETIC STUDIES

2.2.1 Introduction

The thermal decomposition of sodium superoxide is considered to proceed via a two step process as illustrated by the following reactions:

$$2NaO_2 \longrightarrow Na_2O_2 + O_2 \qquad (4)$$

$$Na_2O_2 \longrightarrow Na_2O + 1/2O_2 \qquad (5)$$

If the decomposition proceeds completely to the oxide, 0.75 mole of oxygen is formed for every mole of NaO_2. If, on the other hand, the decomposition stops at the peroxide step, only 0.50 mole of oxygen would be obtained per mole of sodium superoxide under ideal conditions. It is important to note, therefore, that the temperatures at which each of the reactions proceeds are quite different. Sodium superoxide is reported to convert to the peroxide at 250°C,[8] while the oxide is not formed in appreciable quantities from the peroxide until temperatures in excess of 350°C are attained.[12] In selecting catalysts for the decomposition of sodium superoxide, then, it is important that the chosen materials be effective not only in facilitating the conversion of superoxide to peroxide, but also in accelerating the peroxide-oxide transition. In order to produce the maximum amount of oxygen per mole of superoxide, both reactions must proceed.

2.2.2 Experimental Program

Based on the foregoing DTA data, a number of catalyst systems were chosen for isothermal rate studies. Kinetic data were then generated for samples of pure sodium superoxide and sodium peroxide and for samples of both materials containing a number of these catalysts.

Since the simultaneous DTA-TGA plots for sodium superoxide displayed concurrent activity in the 160-170° temperature range, the initial temperature for investigation was set at 160°C. A second temperature of 250°C was also selected for study because TGA data had shown that the major weight loss with sodium superoxide began at this temperature.

In the case of sodium peroxide, all studies were carried out at 250°C since little or no activity was noted below this temperature on the DTA thermograms.

The apparatus utilized for these studies was the same as that employed for the thermal decomposition of potassium ozonide[17], and is shown in Figure 22. At the 160°C level, the temperature was maintained by means of an oil bath. For the runs conducted at 250°C, however, a slight alteration was made in the experimental set up. A reaction tube was made by removing the side arm from the original apparatus. The tube was inserted in an oven and the temperature of the oven was maintained at 250°C by means of a Leeds-Northrup temperature programmer. This apparatus is shown in Figure 23.

The procedure was to bring the reaction vessel to test temperature, purge the system with nitrogen, and drop the sample into the

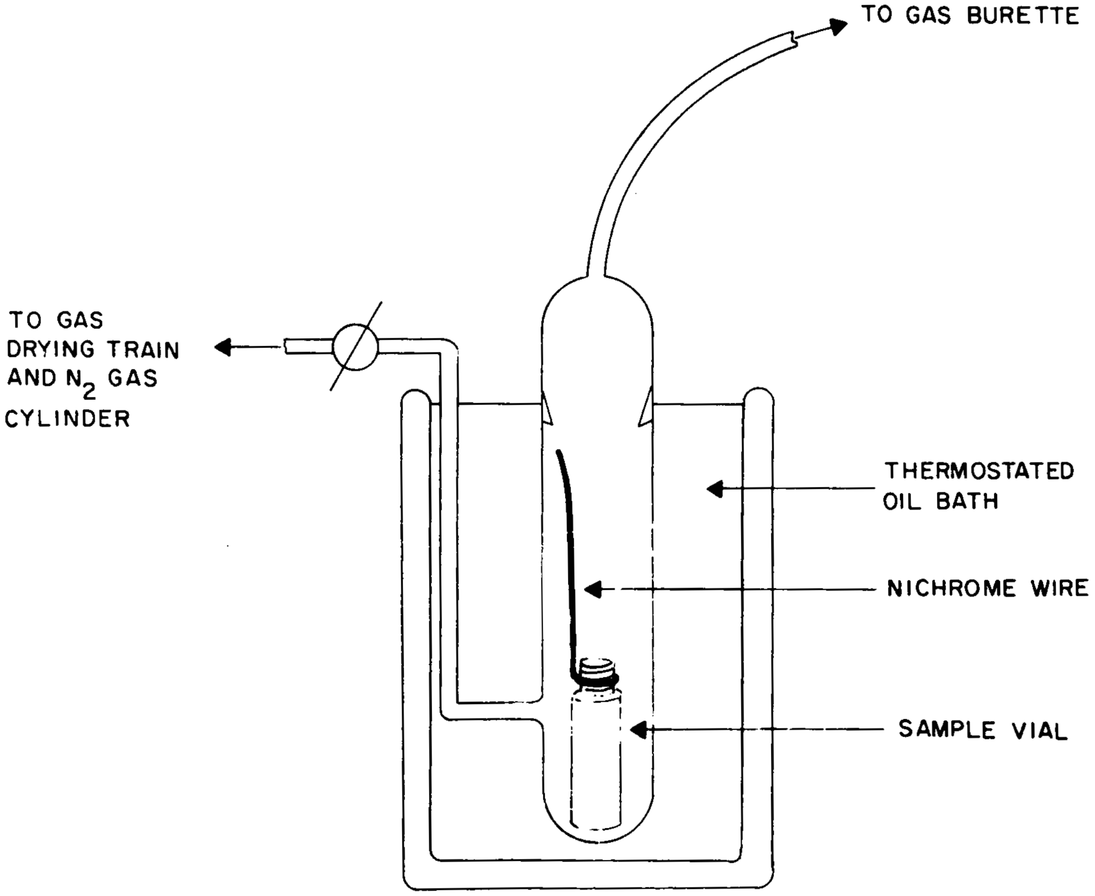


FIGURE 22 APPARATUS USED FOR ISOTHERMAL KINETIC STUDIES OF THE DECOMPOSITION OF SODIUM SUPEROXIDE AT 160°C

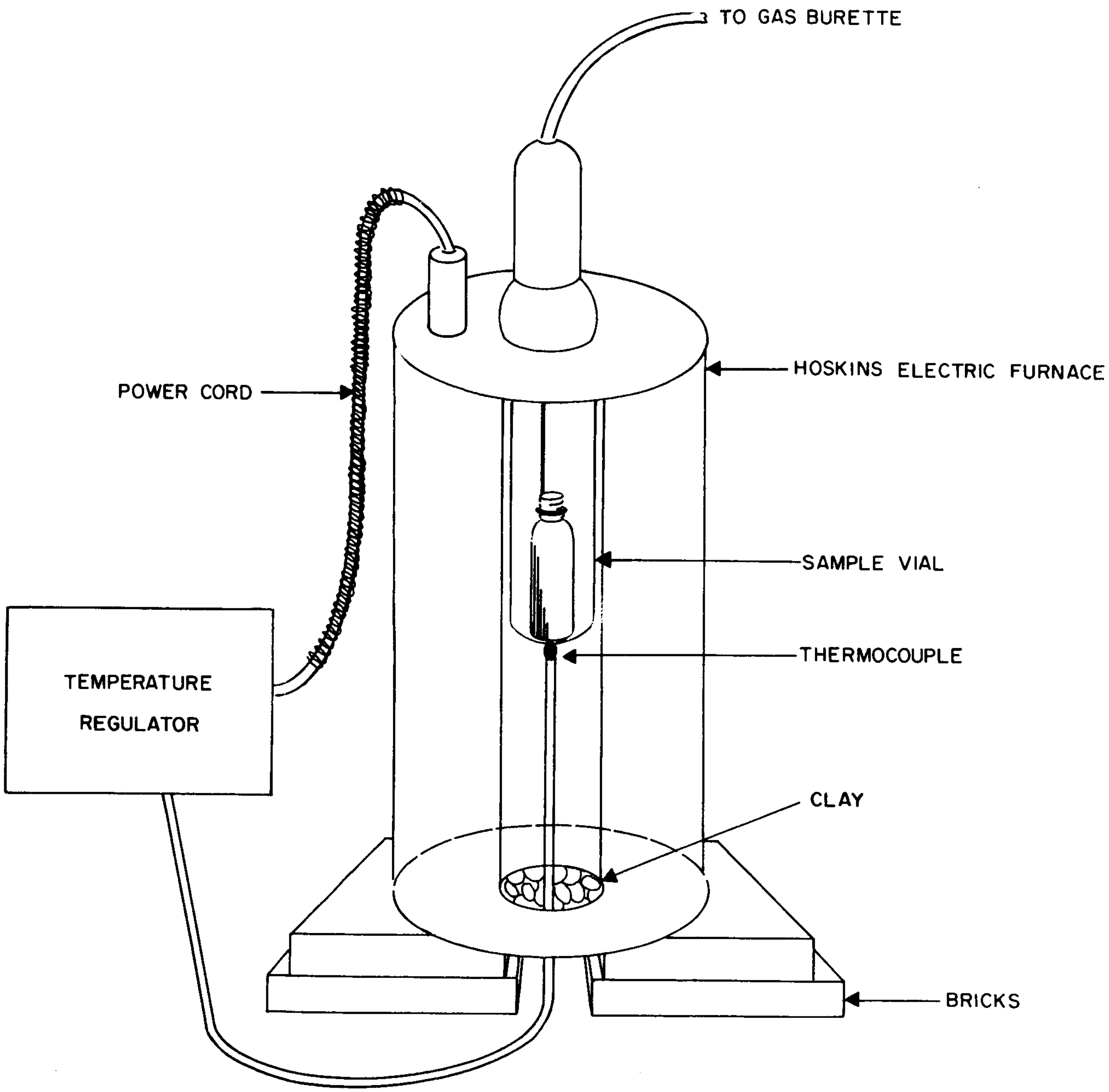


FIGURE 23 APPARATUS FOR THE DECOMPOSITION OF SODIUM SUPEROXIDE AT 250°C

tube by means of a long wire. The course of the reaction was then followed by measuring the volume of oxygen generated by means of a gas burette.

At the end of each run the sample vial was removed from the reaction chamber and cooled to room temperature. The superoxide content remaining in the residue was determined by the Seyb-Kleinberg method.[18]

The thermal decomposition product was further analyzed to determine the amounts of sodium peroxide and sodium oxide remaining. This was accomplished by a standard permanganate titration and determination of the total base content. Finally, the carbonate content of the residue was found by absorbing the carbon dioxide generated from the sample using an Ascarite absorbent.

2.2.3 Results of Kinetic Studies of The Isothermal Decomposition of Sodium Superoxide

The analytical data obtained from the isothermal decomposition of sodium superoxide in combination with various catalysts are summarized in Tables II and III. Analyses were performed on the samples prior to thermal degradation and on the product formed in the decomposition process.

The data show that at both 160° and 250°C the principal product of the decomposition of pure sodium superoxide is sodium peroxide. Some decomposition of the peroxide to form sodium oxide, however, can be seen at both temperature levels. The effect of temperature on the decomposition process is dramatically evident: 49.6% of the superoxide is decomposed in 149 hours at 160°C while 90.47% of the superoxide is decomposed in only 3 hours at 250°C.

2.2.4 Effect of Catalysts On The Decomposition Of Sodium Superoxide

a. Studies at 160°C.

The effect of metallic oxide catalysts on the thermal decomposition of sodium superoxide at 160°C can be seen by examination

TABLE II

SUMMARY OF ANALYTICAL DATA OBTAINED DURING KINETIC STUDIES OF THE ISOTHERMAL DECOMPOSITION OF NaO_2 AT 160°C

COMPOSITION OF SAMPLE	% CATALYST	%NaO_2		%Na_2O_2		%Na_2O		%NaOH		%Na_2CO_3		PERCENT DECOMPOSITION OF		DURATION OF RUN IN HOURS
		Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	NaO_2	Na_2O_2*	
NaO_2 (PURE)	0.0	83.6	49.0	6.5	28.2	0.0	11.9	9.2	10.7	0.6	0.9	49.6	39.5	149
NaO_2 + MnO_2	12.5	73.2	45.8	5.7	4.8	0.0	18.9	8.1	9.1	0.5	1.9	44.4	85.2	145
NaO_2 + V_2O_3	10.0	75.2	39.1	5.8	13.8	0.0	23.2	8.3	9.1	0.5	0.0	52.6	62.9	122
NaO_2 + V_2O_5	18.1	68.5	34.5	5.3	27.9	0.0	0.0	7.5	8.0	0.5	1.0	52.3	13.9	30
NaO_2 + CuPh	20.0	66.9	45.0	5.2	12.4	0.0	4.2	7.4	7.7	0.5	1.8	35.7	46.5	30
NaO_2 + Al_2O_3	12.4	73.3	45.5	5.7	22.0	0.0	7.8	8.1	9.1	0.5	0.0	44.8	32.5	120
NaO_2 Exposed to 100% Humidity for 10 Minutes	0.0	83.6	50.2	6.5	27.6	0.0	6.0	9.2	10.1	0.6	2.3	45.2	24.4	50

*Includes initial Na_2O_2 content plus Na_2O_2 formed from NaO_2 decomposed.

TABLE III

SUMMARY OF THE ANALYTICAL DATA OBTAINED DURING KINETIC STUDIES OF THE ISOTHERMAL DECOMPOSITION OF NaO_2 AT 250°C

COMPOSITION OF SAMPLE	% CATALYST	$\%NaO_2$		$\%Na_2O_2$		$\%Na_2O$		%NaOH		$\%Na_2CO_3$		PERCENT DECOMPOSITION OF		DURATION OF RUN IN HOURS
		Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	NaO_2	Na_2O_2	
NaO_2 (PURE)	0.0	83.6	10.7	6.5	73.0	0.0	2.7	9.2	12.2	0.6	1.0	90.4	8.7	7
$NaO_2 + MnO_2$	8.5	76.5	16.1	5.9	36.5	0.0	15.0	8.4	10.8	0.5	1.0	83.6	44.7	7
$NaO_2 + V_2O_3$	9.9	75.3	20.9	5.9	61.8	0.0	3.2	8.3	10.8	0.5	0.0	78.6	39.1	6
$NaO_2 + V_2O_5$	8.6	76.4	19.2	5.9	54.3	0.0	0.0	8.4	10.8	0.5	3.1	80.5	14.8	7
NaO_2 + CuPh	9.2	75.9	13.7	5.9	37.0	0.0	8.8	8.4	12.6	0.5	0.0	88.0	53.7	6
NaO_2 Exposed to H_2O for 15 Minutes	0.0	83.6	10.6	6.5	72.6	0.0	0.0	9.2	12.4	0.6	2.8	90.6	10.5	6

of the data compiled in Table II. The percent decompositions for both sodium superoxide and sodium peroxide are tabulated for each of the catalyzed mixtures. In computing the value of the latter, the amount of Na_2O_2 formed in the decomposition of the superoxide, plus the amount of Na_2O_2 originally present, were taken together as the initial peroxide concentration.

Of the catalysts investigated, the two vanadium oxides appeared to accelerate the decomposition of superoxide, while three of the compounds (manganese dioxide, aluminum oxide and copper polyphthalocyanine) actually seemed to retard the decomposition process. With these latter materials, less decomposition was noted with the catalyzed samples than with pure sodium superoxide.

In the case of the vanadium catalysts, the lower oxide, V_2O_3, effected a higher percent decomposition, not only of superoxide,but also of peroxide. With this catalyst, therefore, the decomposition reaction proceeds to the oxide to a significant extent. The pentavalent vanadium oxide, V_2O_5, on the other hand, resulted mainly in the formation of sodium peroxide with very little decomposition to the oxide being noted. On the basis of this data, therefore, and at this temperature, vanadium(III) oxide appears to be the most effective catalyst for generating oxygen by the thermal decomposition of sodium superoxide.

It is interesting to note that manganese dioxide and, to a lesser extent, the phthalocyanine catalyst, although showing decreased activity in decomposing superoxide, nevertheless displayed exceptional ability in facilitating the decomposition of sodium peroxide to sodium oxide. Thus, despite the smaller amount of superoxide decomposition, these catalysts must be considered among the more active because of the extent to which the decomposition reaction goes to completion (i.e. to the oxide). In contrast, the aluminum oxide catalyst apparently inhibits both the superoxide and peroxide decompositions.

It should be pointed out, that two of the catalytic materials, the polyphthalocyanine and vanadium (V) oxide, were allowed to react for only 30 hours while the decompositions of the other samples were conducted for at least 120 hours Comparison of the results obtained with these two materials, therefore, may not be valid.

The kinetic curves illustrating the volumes of oxygen produced by the above mentioned systems as a function of time are given in Figures 24 through 29. It is noted that on the basis of the volume of oxygen produced per gram of NaO_2, the catalysts in order of effectiveness are: $V_2O_3 > V_2O_5 > MnO_2 >$ CuPh. The rate constants, determined by constructing tangents to the curves at selected points, are nearly equal ($k_1 \approx 0.5$; $K_2 \approx 0.2$) at this temperature. Because of the small degree of conversion of superoxide occurring at 160°C with all of the systems tested(ca.50% conversion in > 100 hours), further work at this temperature was discontinued and attention was focused on higher reaction temperatures.

b. Isothermal Studies at 250°C

The analytical data obtained form the decomposition of sodium superoxide at 250°C are compiled in Table III. Immediately obvious is the dramatic increase in the rate of the decomposition at the higher temperature. At the 160°C level, superoxide decompositions of 35-50% were realized only after more than 100 hours of reaction; at 250°C, 80-90% of the superoxide was decomposed in 2-3 hours. In light of this increased activity, it is unusual to note that, based on the percent decomposition given in Table III, all of the catalysts tested appeared to inhibit the decomposition of sodium superoxide. In contrast, the decomposition of sodium peroxide appeared to be enhanced by the presence of the catalysts. Again the manganese dioxide and copper polyphthalocyanine catalyst showed exceptional ability in facilitating the decomposition of peroxide to the oxide. In the case of the phthalocyanine,

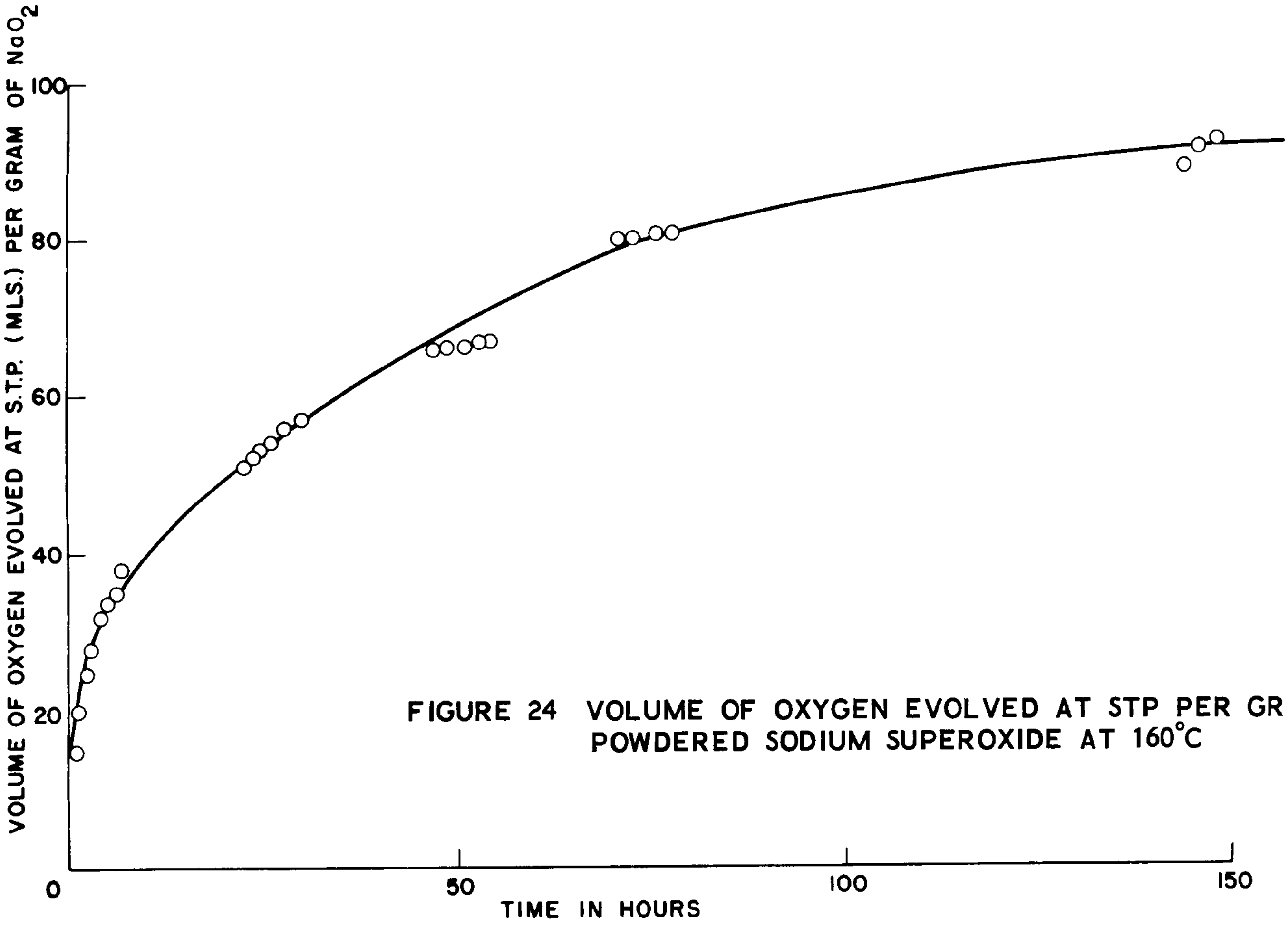


FIGURE 24 VOLUME OF OXYGEN EVOLVED AT STP PER GRAM OF POWDERED SODIUM SUPEROXIDE AT 160°C

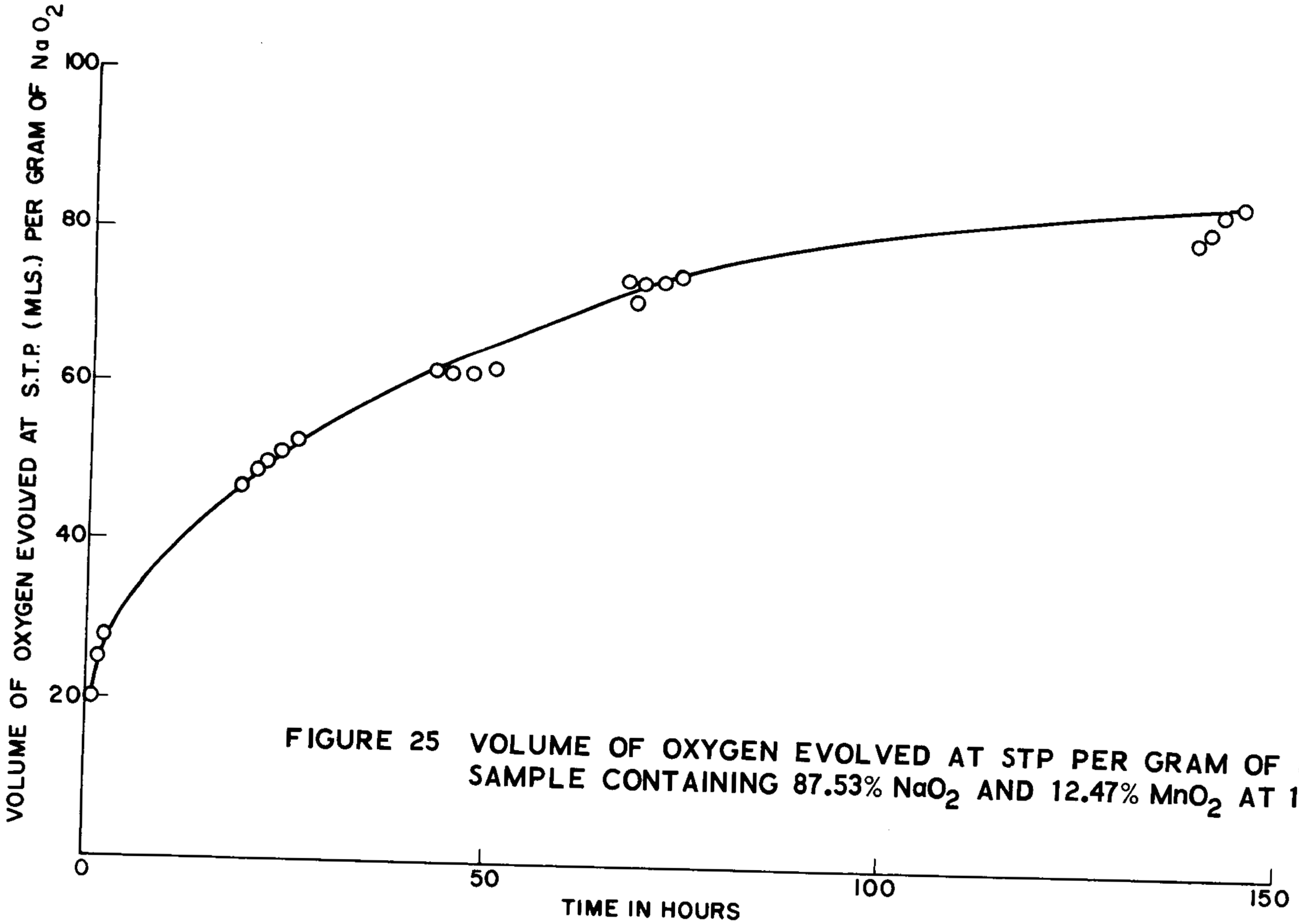


FIGURE 25 VOLUME OF OXYGEN EVOLVED AT STP PER GRAM OF NaO_2 IN A SAMPLE CONTAINING 87.53% NaO_2 AND 12.47% MnO_2 AT 160°C

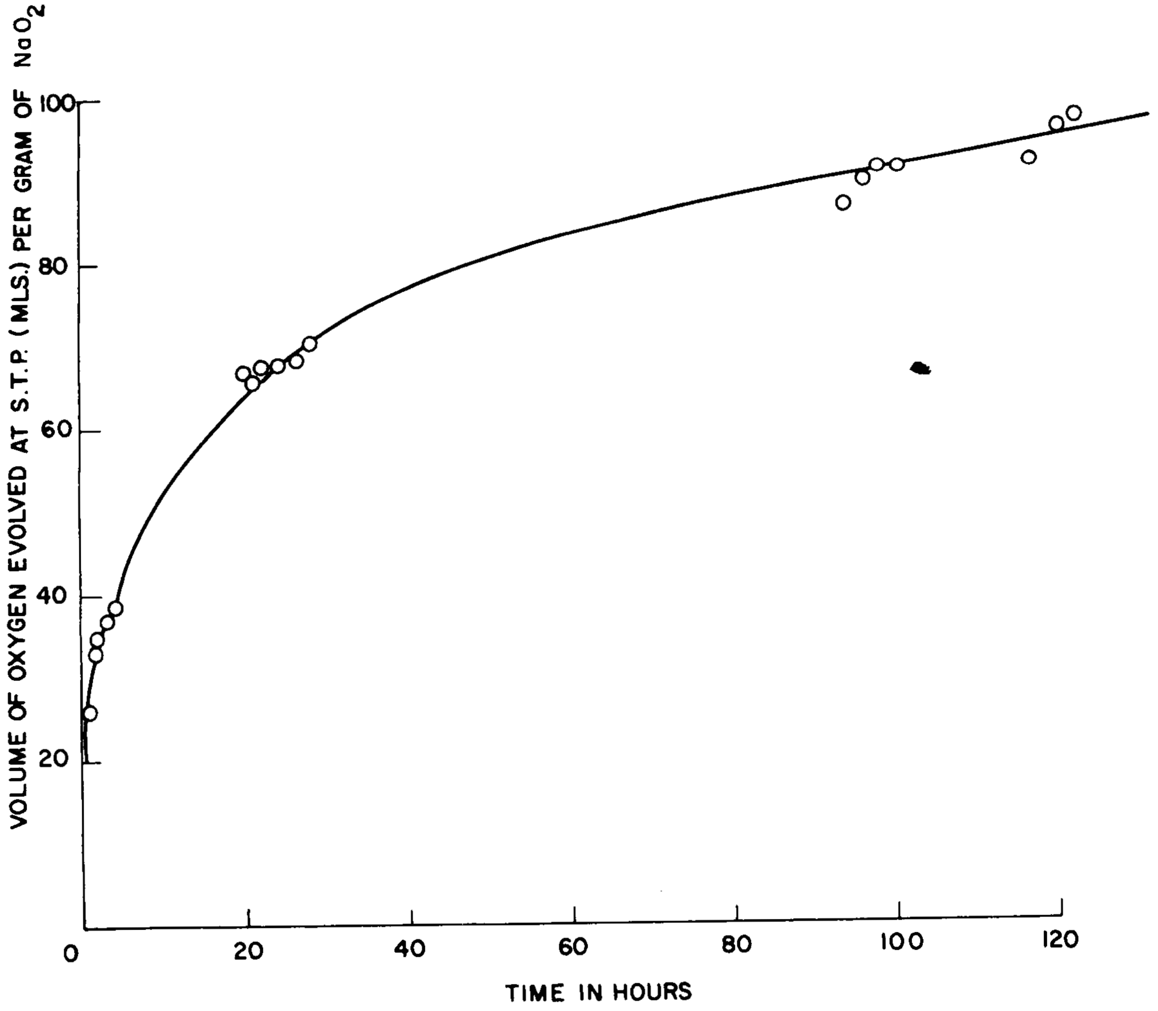


FIGURE 26 VOLUME OF OXYGEN EVOLVED AT STP PER GRAM OF NaO_2 IN A SAMPLE CONTAINING 90.00% NaO_2 AND 10.00% V_2O_3 AT 160°C

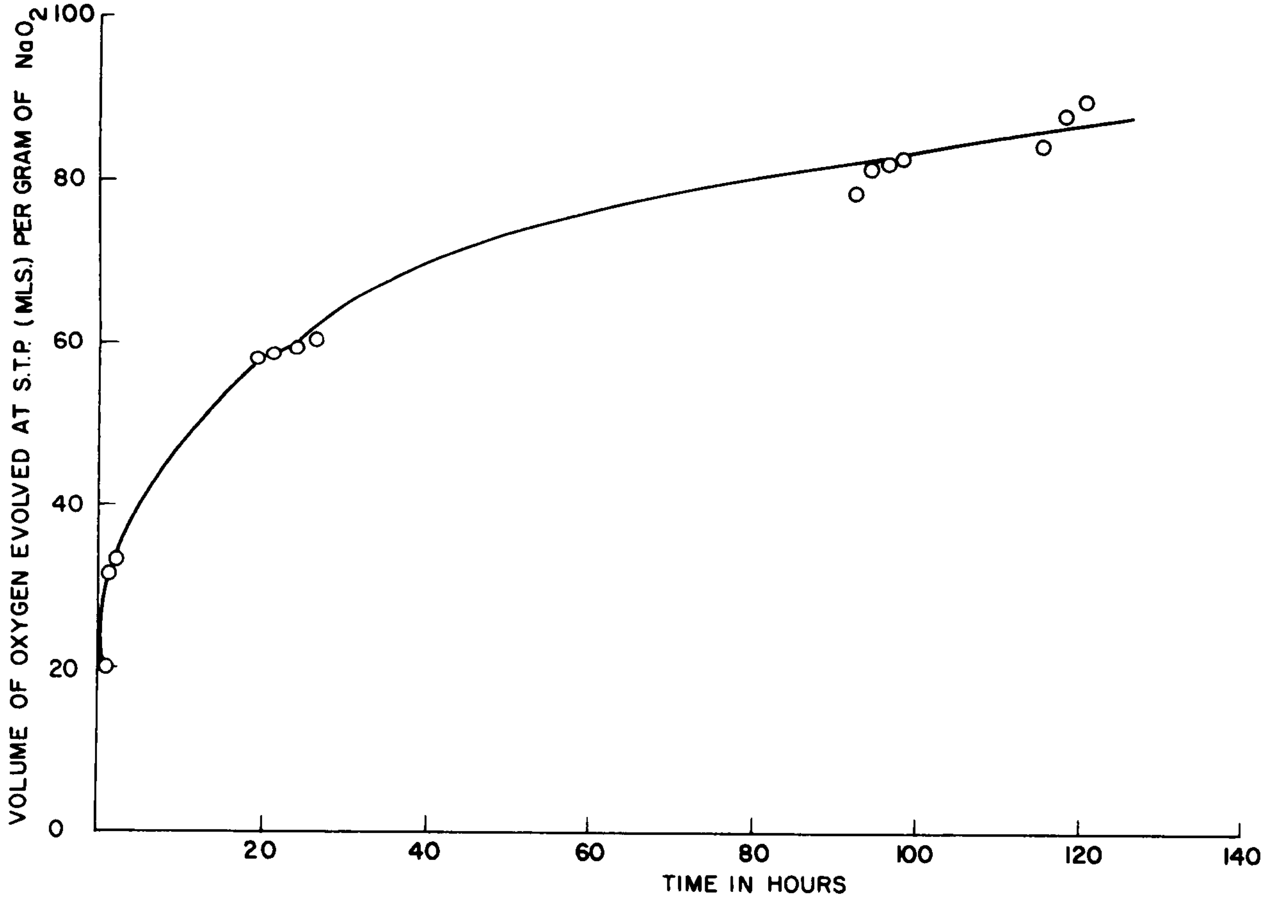


FIGURE 27 VOLUME OF OXYGEN EVOLVED AT STP PER GRAM OF NaO_2 IN A SAMPLE CONTAINING 87.65% NaO_2 AND 12.35% Al_2O_3 AT 160°C

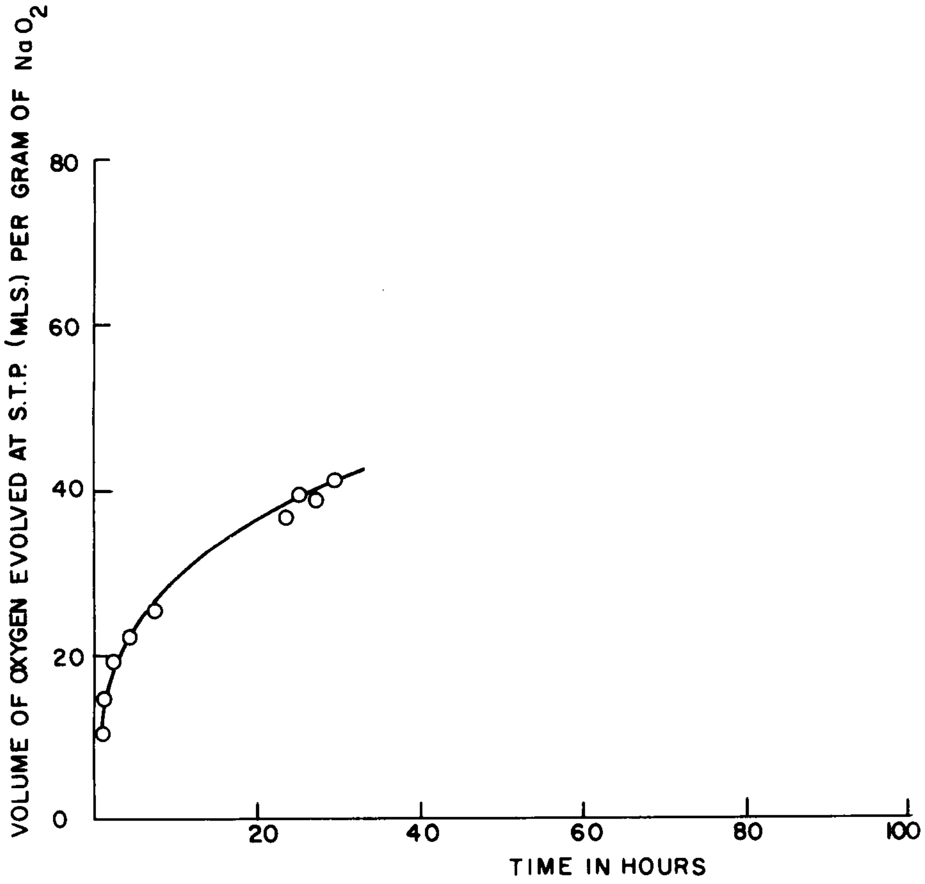


FIGURE 28 VOLUME OF OXYGEN EVOLVED AT STP PER GRAM OF NaO_2 IN A SAMPLE CONTAINING 81.94% NaO_2 AND 18.06% V_2O_5 AT 160°C

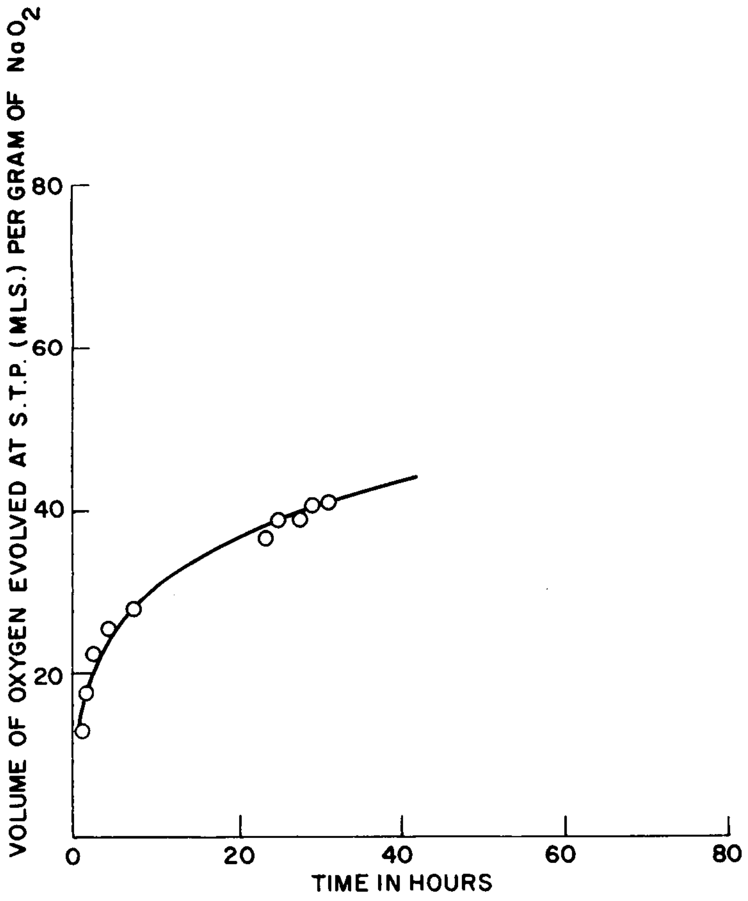


FIGURE 29 VOLUME OF OXYGEN EVOLVED AT STP PER GRAM OF NaO_2 IN A SAMPLE CONTAINING 80.0% NaO_2 AND 20.00% COPPER POLYPHTHALOCYANINE AT 160°C

moreover, the superoxide decomposition was only slightly less than that of the pure sodium superoxide. Interestingly enough, the two vanadium oxides which displayed the highest superoxide decompositions at 160°C., resulted in the lowest conversion at 250°C.

In seeking an explanation of the inhibitory action of these oxides at 250°C, it is recalled that strong exotherms were observed on the DTA thermograms (Figures 8 and 9) of these catalyzed systems in the temperature range in point. It is possible, therefore, that at the higher temperature an exothermic reaction may take place between the metal oxide and sodium superoxide to form a complex of the type $NaO_2.M_xO_y$. The thermal decomposition of such an adduct might be expected to proceed at a slower rate than that of the uncomplexed superoxide, thus resulting in a lower percent decomposition being recorded with the oxide catalyst.

In addition to the DTA data, other evidence for reaction (and/or the formation of such complexes) under the conditions employed here was the development of the dark blue color encountered with the NaO_2-MnO_2 system. Still further, a number of authors have reported the formation of complexes of general type $MO_2.M_xO_y$ under similar conditions.[12]

In attempting to assess the relative value of the catalysts examined in this research, it is not sufficient to consider only the data concerning the extent of superoxide and peroxide decomposition. Rather, the goal of this work--to utilize the thermal decomposition process of solid superoxides for the controlled, efficient generation of oxygen gas--must be borne in mind. The real criterion for judging catalyst worth, therefore, is the actual yield of oxygen and the rate at which the gas is produced. The data in Table IV represent gravimetric and volumetric results of the amounts of oxygen produced by the various catalyzed samples. Good agreement is noted between the gravimetric and volumetric determination of oxygen yields in all cases except one. With the copper polyphthalocyanine catalyst, a percent conversion to oxygen of nearly

TABLE IV

SUMMARY OF GRAVIMETRIC AND VOLUMETRIC DATA ON THE OXYGEN EVOLUTION OBTAINED DURING ISOTHERMAL DECOMPOSITION OF CATALYZED NaO_2 MIXTURES AT 250°C

SYSTEM	CATALYST CONCENTRATION %	GRAVIMETRIC DATA					VOLUMETRIC DATA				DURATION OF EXPERIMENT IN HOURS
		Wt. of NaO_2 in Sample (grams)	Wt. of Oxygen Produced (Wt. Loss)	Theoretical(b) Weight of O_2	% Oxygen(b) Produced		Total Volume of O_2 Produced at S.T.P. (Ml)	Theoretical(b) Volume of O_2 S.T.P^{at} (Ml)	% Oxygen(b) Produced		
					Conversion	Yield			Conversion	Yield	
NaO_2	0.0	0.5361	0.1333	0.2339	57.0	63.0	92.4	163.7	56.4	62.4	7
NaO_2 + CuPh(a)	9.2	0.3189	0.1292	0.1390	92.9	>100	55.3	97.30	56.9	64.6	6
NaO_2 + Mno_2	8.5	0.3467	0.0831	0.1512	55.0	65.7	62.7	105.8	59.3	70.9	7
NaO_2 + V_2O_3	9.9	0.3616	0.1010	0.1577	64.0	82.7	76.3	110.4	69.1	87.9	6
NaO_2 + V_2O_5	8.6	0.3938	0.1060	0.1717	61.7	76.6	80.4	120.2	66.9	83.1	7
NaO_2 + H_2O	0.0	0.3053	0.0942	0.1532	61.5	67.9	67.9	107.2	63.3	68.8	6

(a) Polymeric Copper Phthalocyanine; (b) Based on equation: $2NaO_2 \longrightarrow Na_2O + 3/2\ O_2$

100% is observed based on the gravimetric data, while the volumetric data indicates a conversion of only 56.9%. The gravimetric results are obviously in error since the analytical data (Table III) have shown that only an 88.0 percent decompostion of superoxide is achieved with this catalyst. A plausible explanation for the abnormally large weight loss observed is that the catalyst itself entered into the reaction. The phthalocyanine polymer is a very large organic molecule which in all probability contains oxidizable sites (e.g. side groups). It is entirely conceivable, therefore, that at this high temperature (250°C), and in the presence of such a powerful oxidizing agent, some oxidation might take place. It is more difficult to explain why the volumetric results are not also abnormally high, in as much as any oxidation might be expected to result in the production of volatile materials. It is recalled, however, that the fluid in the gas burrette is an organic ester (dibutyl phthalate). If the products of the oxidation were low molecular weight organic compounds, some solubility in dibutyl phthalate might be expected, and thus little change in the volumetric results would occur. The only other explanation for the anomalous data obtained with the phthalocyanine is experimental error.

There is a possibility that the results reported for the manganese dioxide catalyzed sample may be somewhat low in light of the high conversion of both superoxide and peroxide previously observed with this catalyst (Table III). It has to be recalled that at about 250°C a reaction was observed which resulted in the formation of a blue-colored product. If the stability of this product is such that it decomposes more slowly than the uncomplexed superoxide, then both the weight loss and the volume of oxygen produced would be decreased. Perhaps this catalyst would be more effective at temperatures slightly below 250°C where no color development (hence reaction) has been observed.

Since, in addition to the yield of oxygen, the rate of gas evolution is also an important variable, the kinetic curves and first order rate plots for the systems studied have been prepared (Figures 30 through 40). The data taken from these plots are summarized in Table V. It is seen that the reactions with all systems were essentially over in three hours. It is interesting to note that the phthalocyanine catalyzed sample, although it produced the smallest volume of oxygen per gram of superoxide, gave the most rapid reaction rate observed. Perhaps this catalyst should be investigated at lower temperatures in order to determine if reaction of the catalyst with the superoxide could be avoided and hence the amount of oxygen increased.

Based on the data of Tables III, IV and V, therefore, the order of effectiveness of the catalysts at 250°C is:

$$V_2O_3 > MnO_2 \simeq V_2O_5 > CuPh.$$

2.2.5. Effect of Absorbed Water on The Decomposition of Sodium Superoxide

The catalytic effect of absorbed water vapor on the decomposition of sodium superoxide was also investigated. The data from these studies are included in Tables II through V. At 160°C, the preconditioned sample decomposed to a lesser extent than untreated sodium superoxide, while at 250°C the percent decompositions were about the same for both samples. The yield of oxygen from the preconditioned sample, moreover, is only slightly greater than that from the untreated superoxide (Table IV). The kinetic data and the rate plot for the preconditioned sample confirm that, although the total volume of oxygen generated per gram of superoxide is somewhat larger than that obtained from pure sodium superoxide, the rate of oxygen production is slightly lower. The effect of preconditioning sodium superoxide by exposure to moisture, therefore, does not appear to affect significantly the oxygen producing ability of the pure compound.

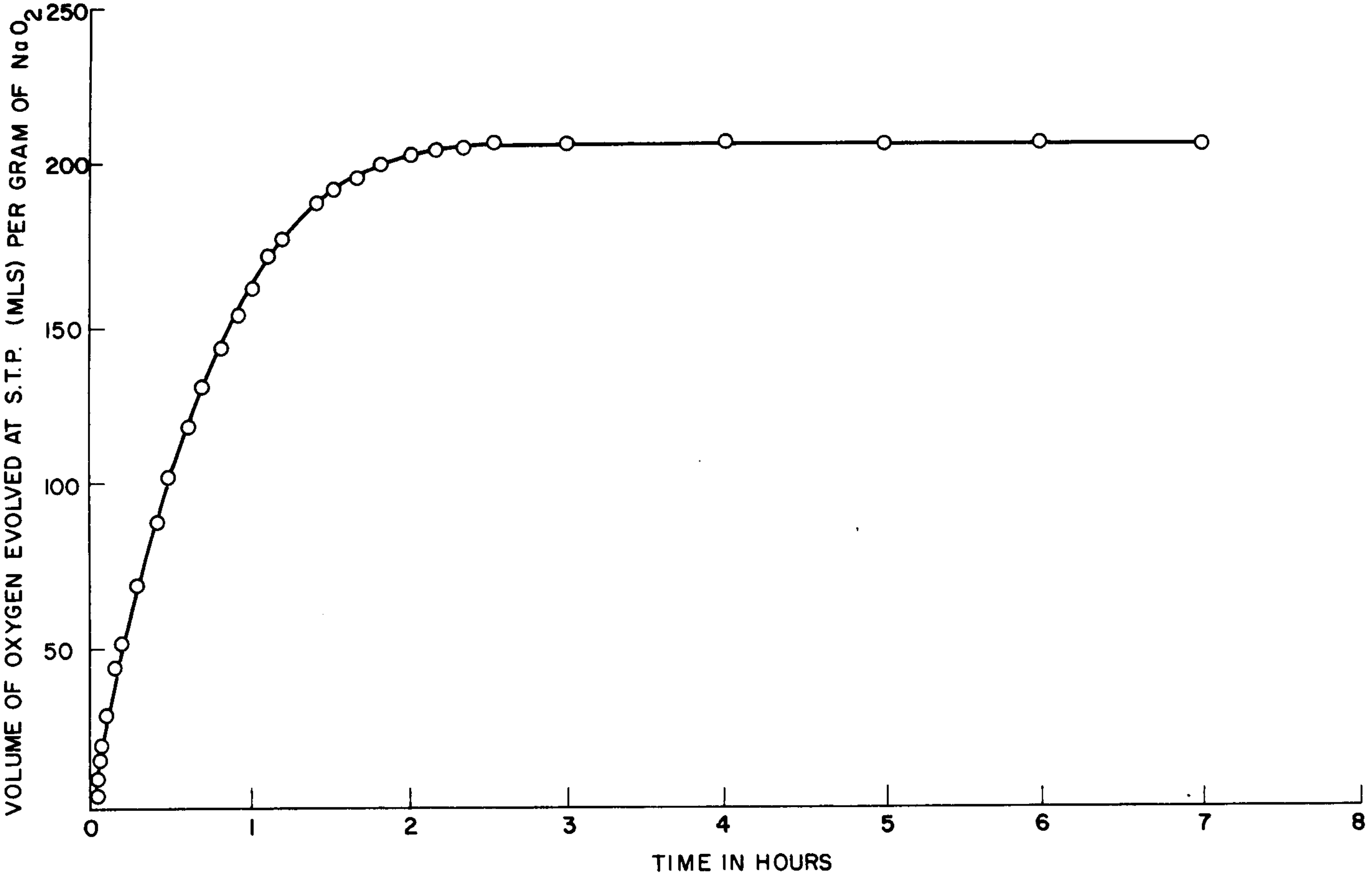


FIGURE 30 VOLUME OF OXYGEN EVOLVED AT STP PER GRAM OF POWDERED SODIUM SUPEROXIDE AT 250°C

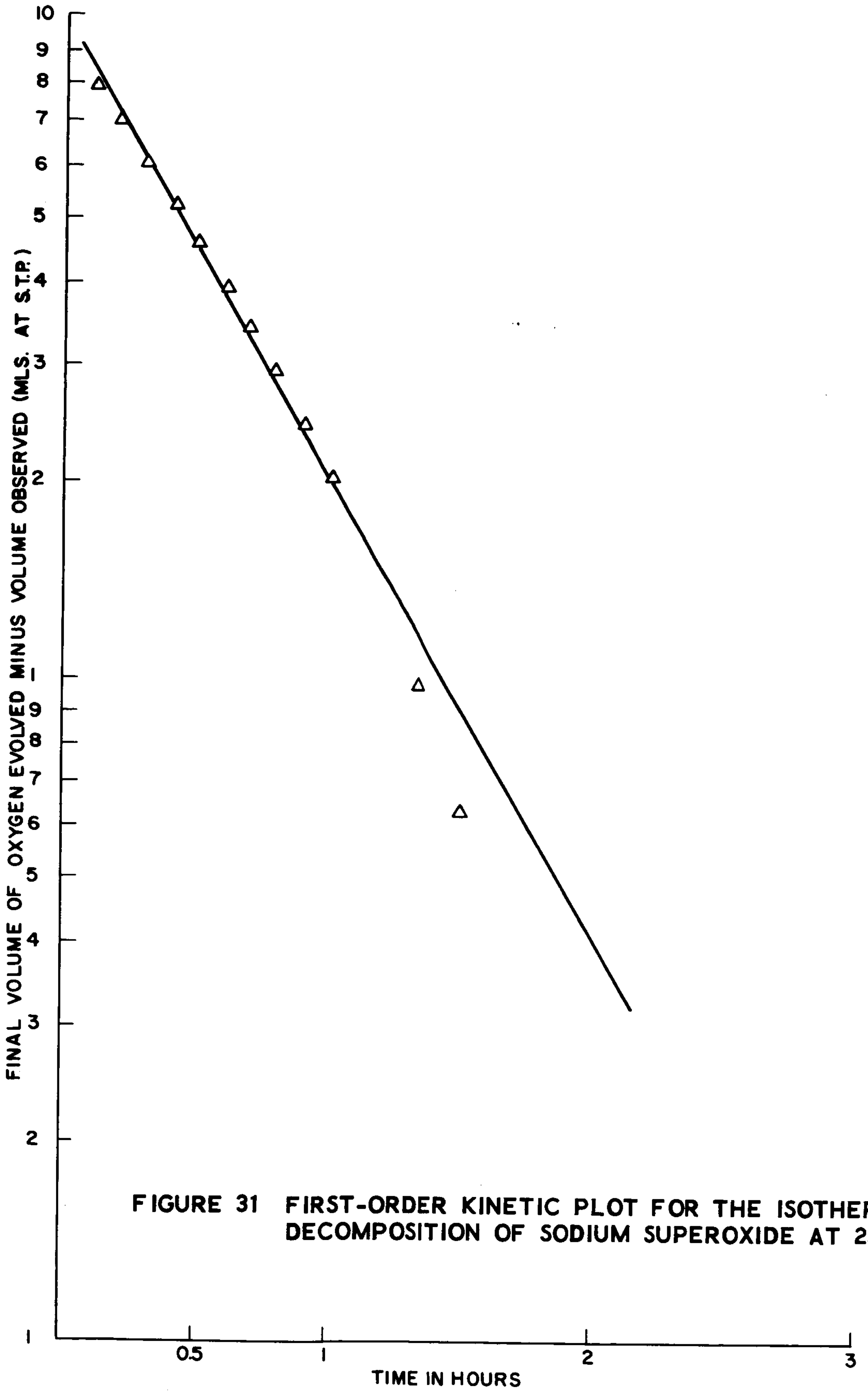


FIGURE 31 FIRST-ORDER KINETIC PLOT FOR THE ISOTHERMAL DECOMPOSITION OF SODIUM SUPEROXIDE AT 250°C

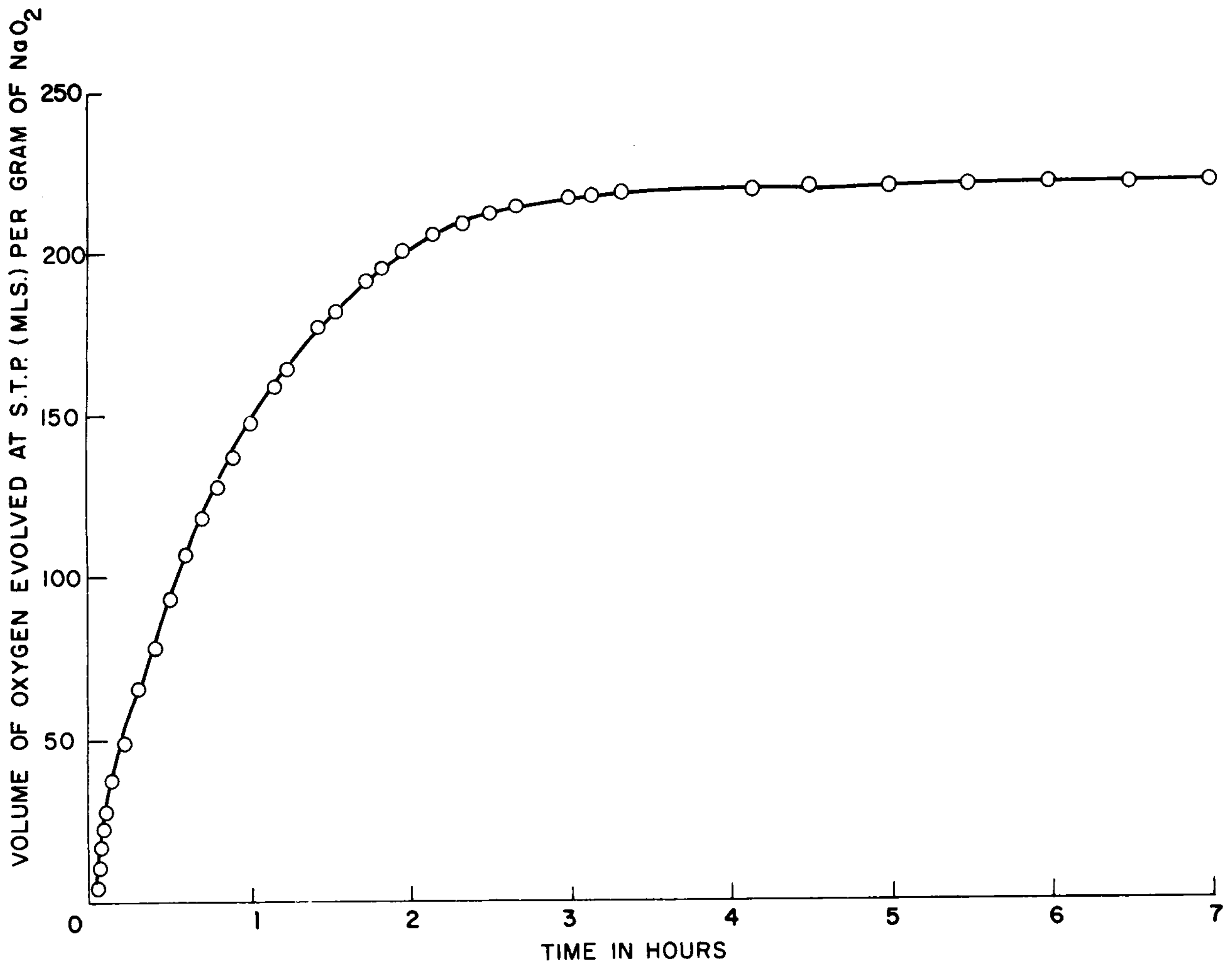


FIGURE 32 VOLUME OF OXYGEN EVOLVED AT STP PER GRAM OF NaO_2 IN A SAMPLE CONTAINING 76.4% NaO_2 AND 8.6% V_2O_5 AT 250°C

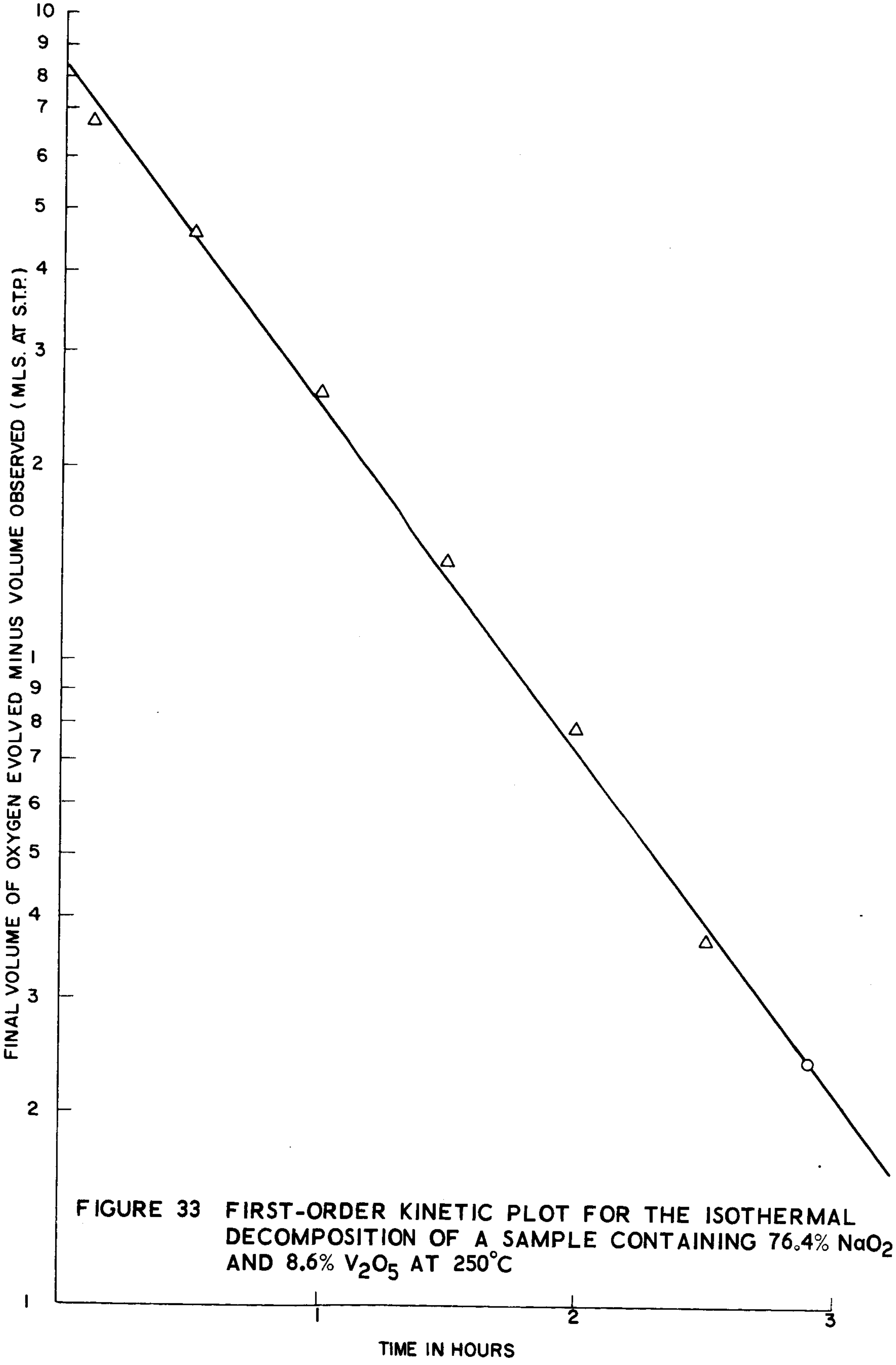


FIGURE 33 FIRST-ORDER KINETIC PLOT FOR THE ISOTHERMAL DECOMPOSITION OF A SAMPLE CONTAINING 76.4% NaO_2 AND 8.6% V_2O_5 AT 250°C

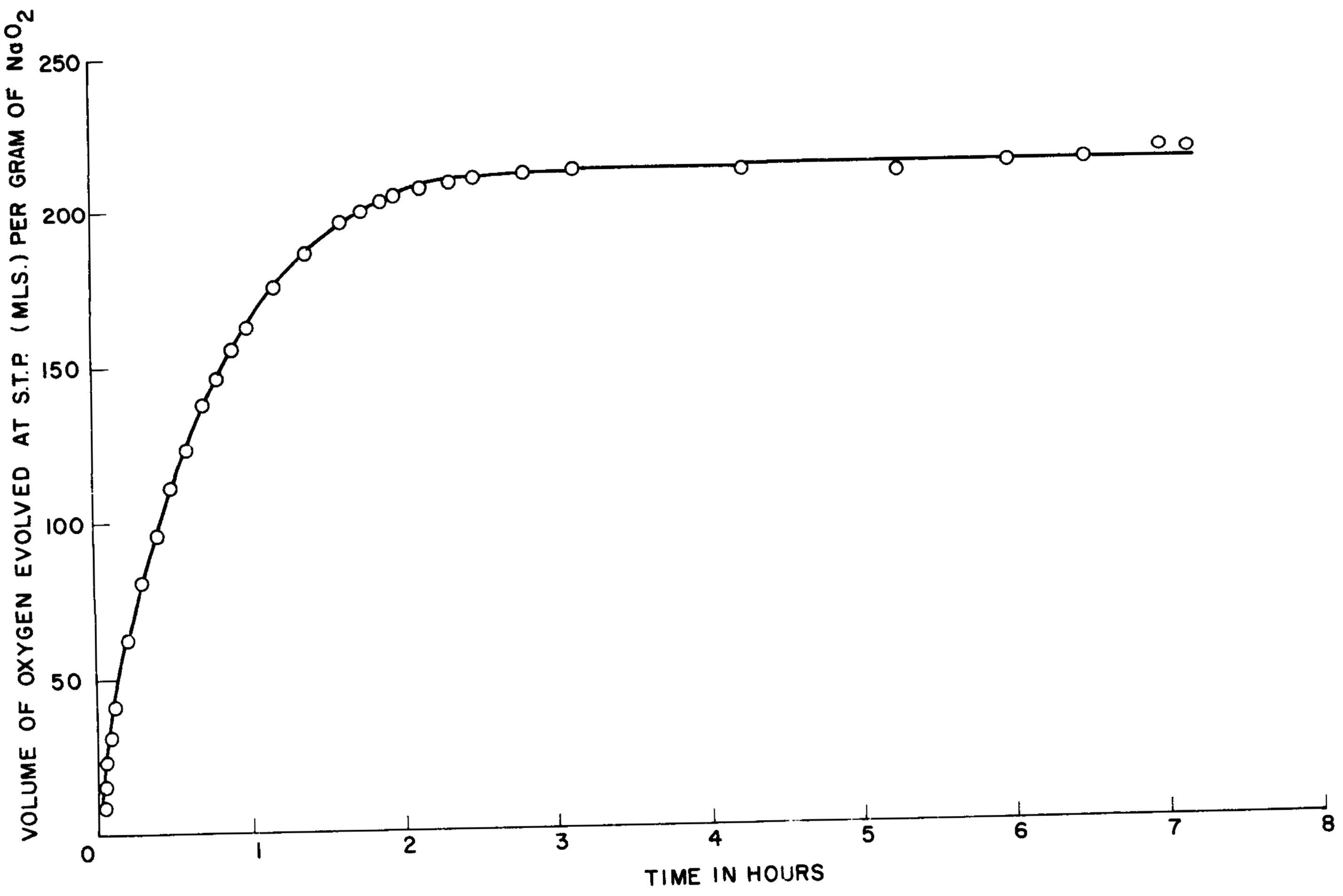
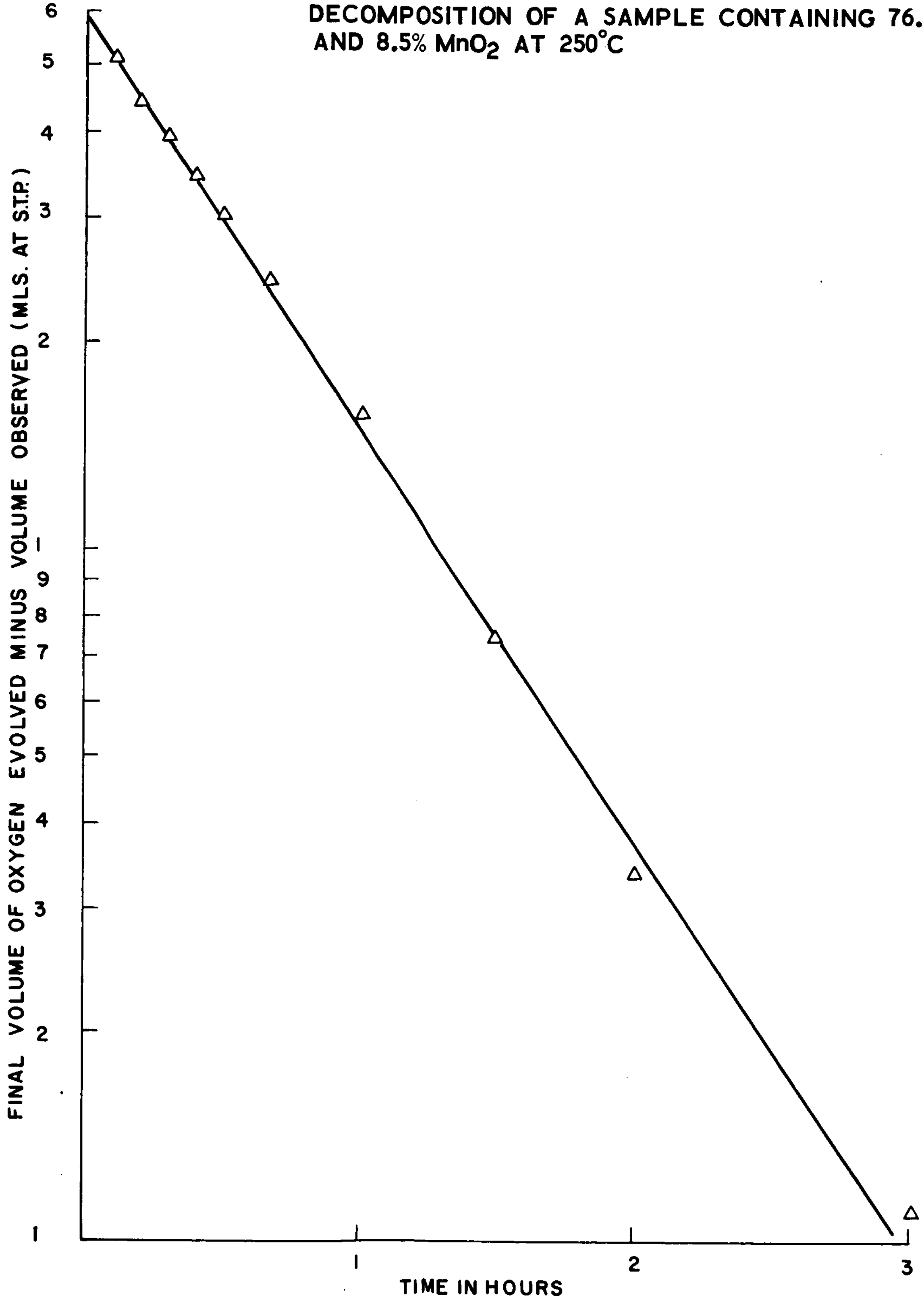


FIGURE 34 VOLUME OF OXYGEN EVOLVED AT STP PER GRAM OF NaO_2 IN A SAMPLE CONTAINING 76.5% NaO_2 AND 8.5% MnO_2 AT 250°C

FIGURE 35 FIRST-ORDER KINETIC PLOT FOR THE ISOTHERMAL DECOMPOSITION OF A SAMPLE CONTAINING 76.5% NaO_2 AND 8.5% MnO_2 AT 250°C



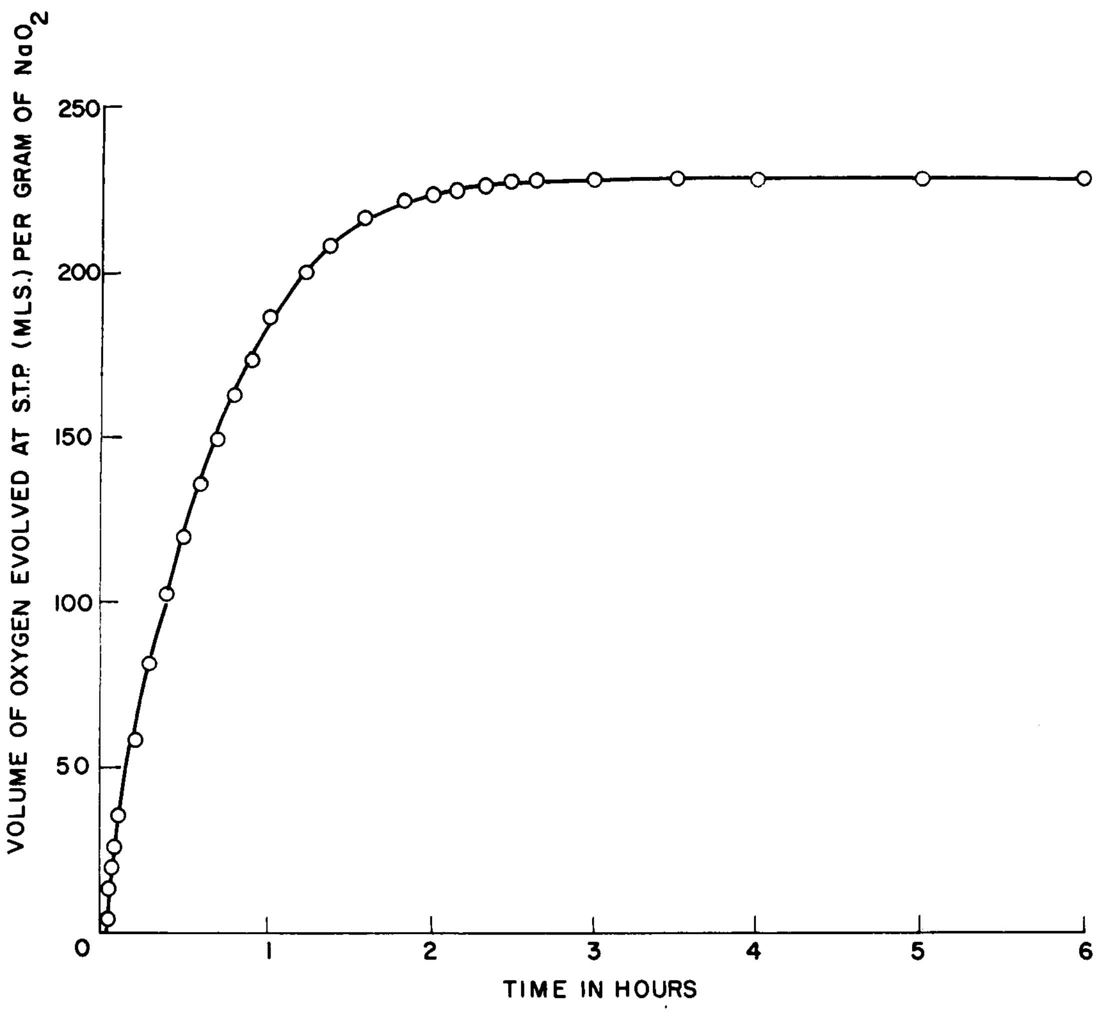


FIGURE 36 VOLUME OF OXYGEN EVOLVED AT STP PER GRAM OF NaO_2 IN A SAMPLE CONTAINING 75.3% NaO_2 AND 9.9% V_2O_3 AT 250°C

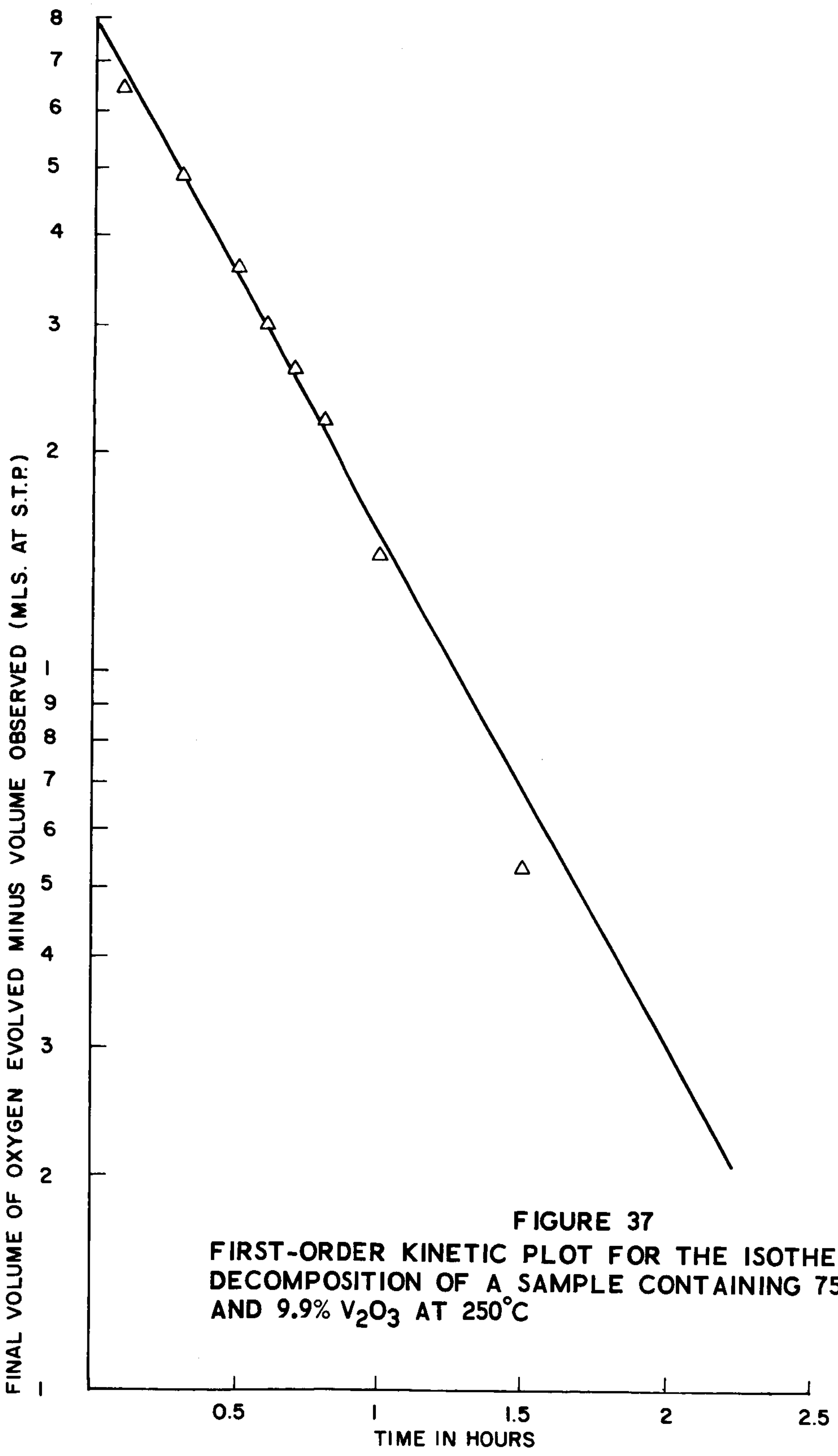


FIGURE 37
FIRST-ORDER KINETIC PLOT FOR THE ISOTHERMAL DECOMPOSITION OF A SAMPLE CONTAINING 75.3% NaO_2 AND 9.9% V_2O_3 AT 250°C

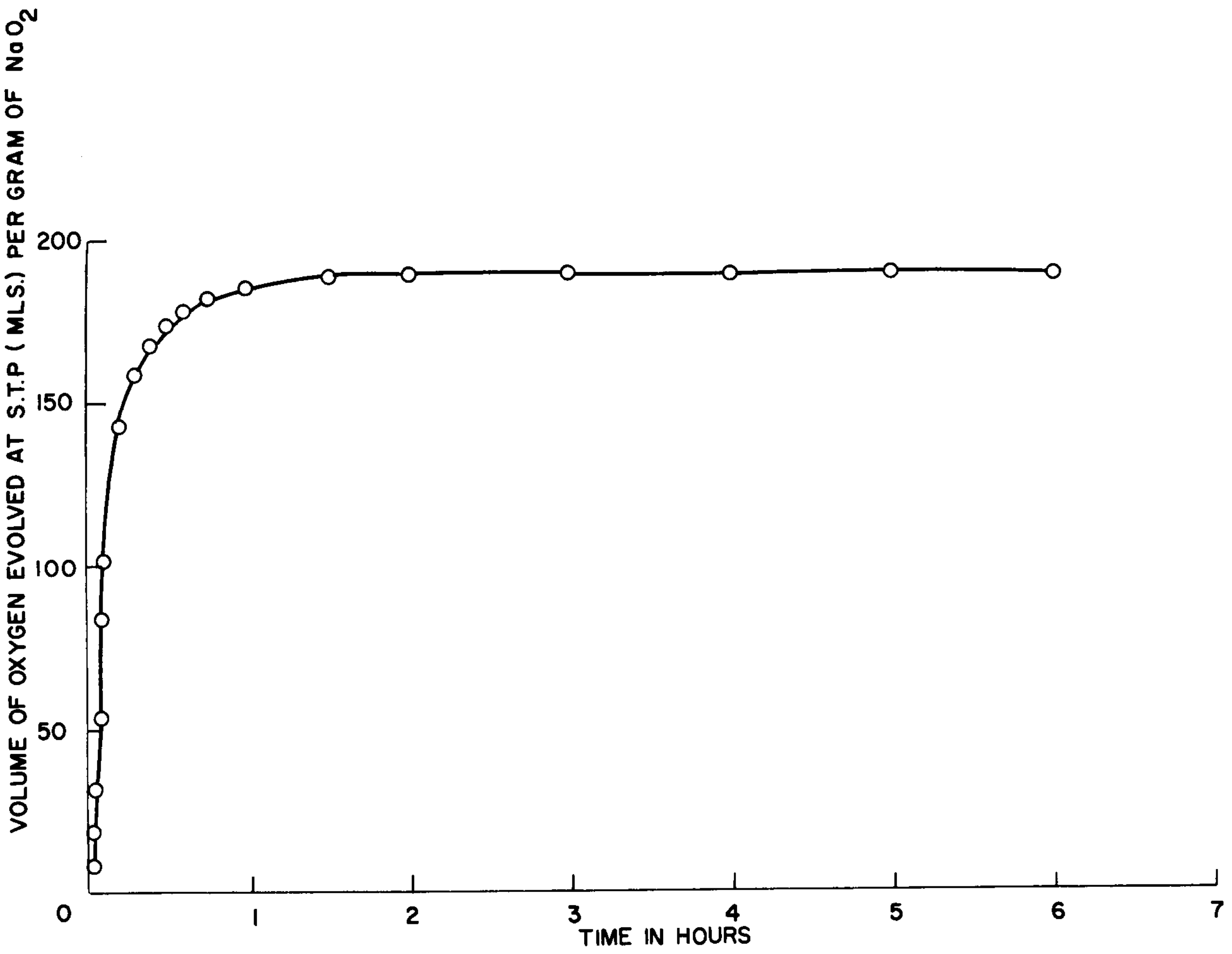
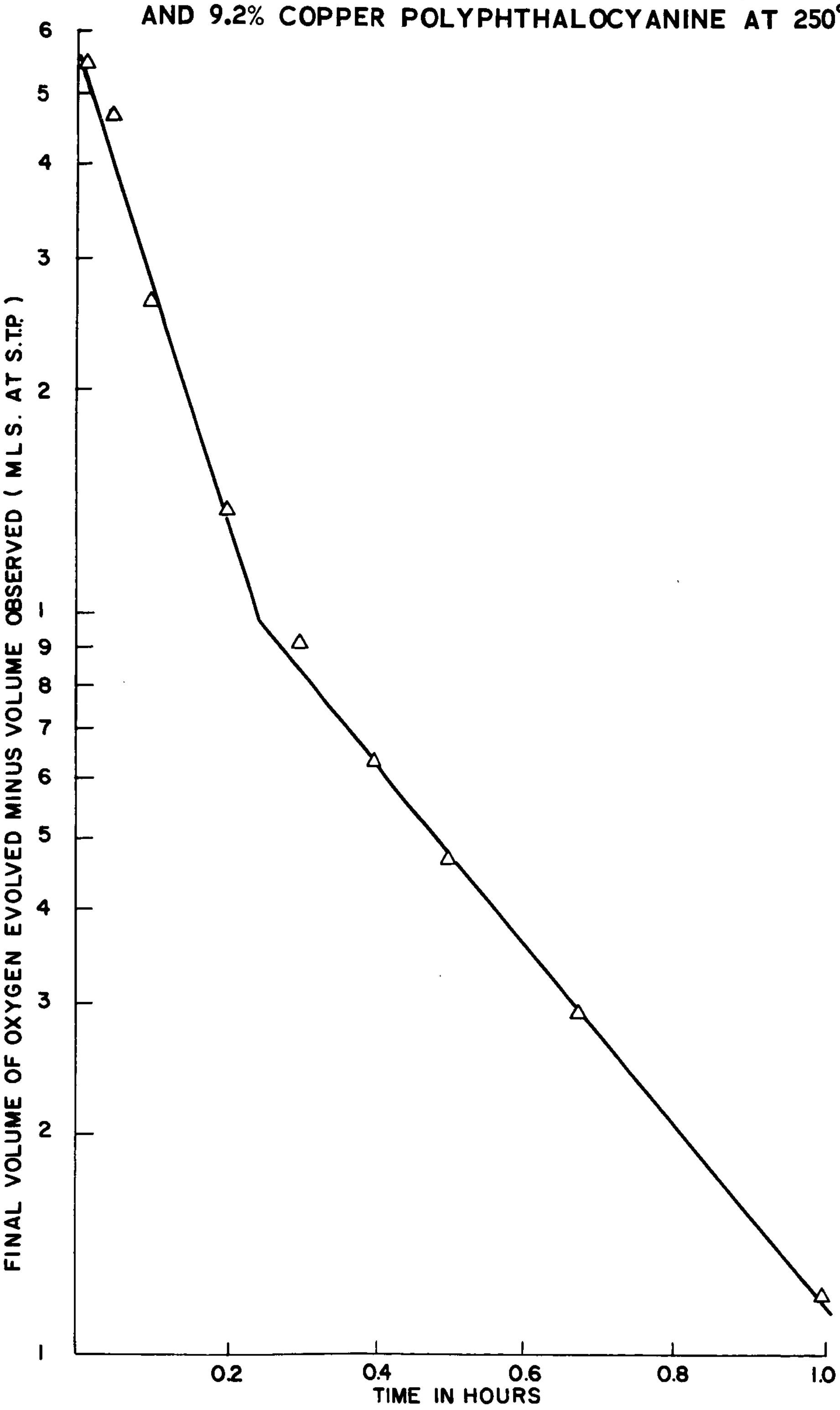


FIGURE 38 VOLUME OF OXYGEN EVOLVED AT STP PER GRAM OF NaO_2 IN A SAMPLE CONTAINING 75.9% NaO_2 AND 9.2% COPPER POLYPHTHALOCYANINE AT 250°C

FIGURE 39 FIRST-ORDER KINETIC PLOT FOR THE ISOTHERMAL DECOMPOSITION OF A SAMPLE CONTAINING 75.9% NaO_2 AND 9.2% COPPER POLYPHTHALOCYANINE AT 250°C



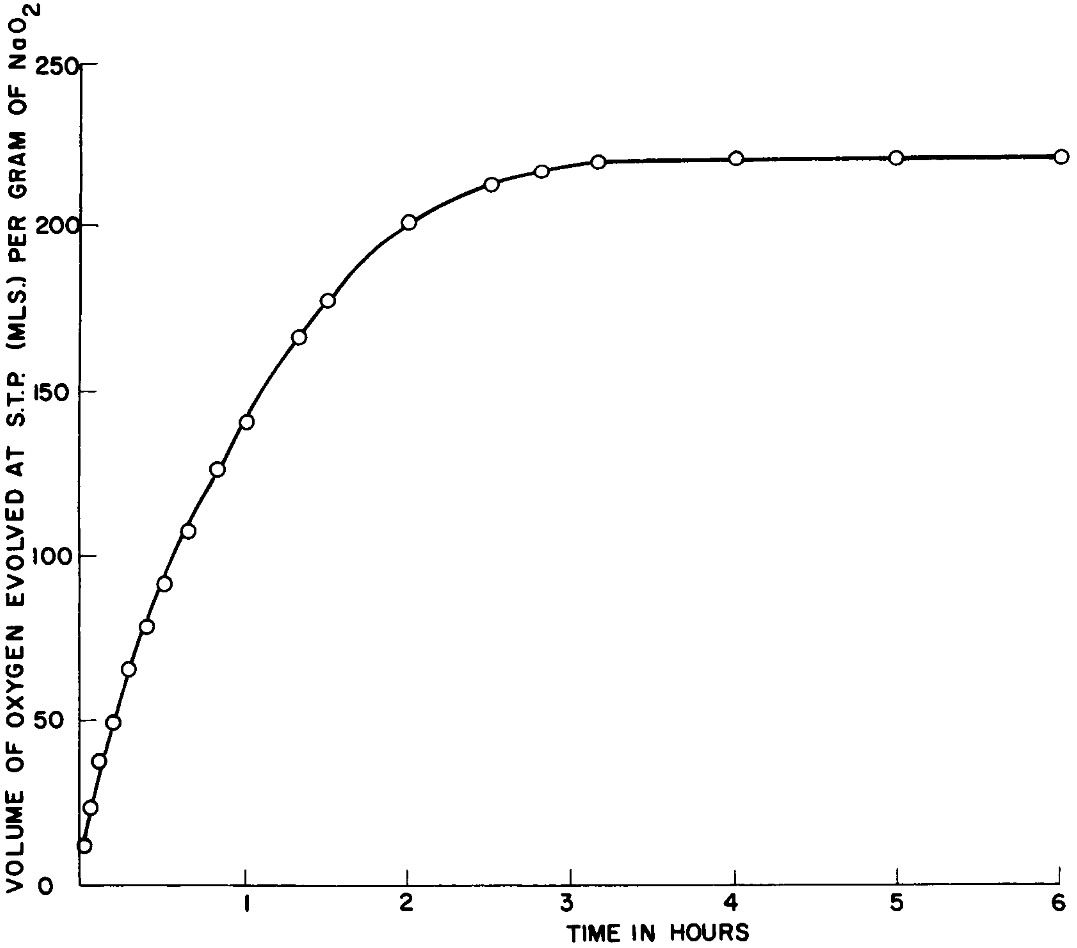


FIGURE 40 VOLUME OF OXYGEN PRODUCED AT STP PER GRAM OF SODIUM SUPEROXIDE EXPOSED TO 100% HUMIDITY FOR 15 MINUTES PRIOR TO REACTION AT 250°C

TABLE V

SUMMARY OF KINETIC DATA OBTAINED DURING ISOTHERMAL DECOMPOSITION OF NaO_2 SYSTEMS AT 250°C

SYSTEM	TOTAL VOLUME (mls) of O_2 EVOLVED/GRAM of NaO_2 (a)	% of TOTAL VOLUME of O_2 EVOLVED AFTER:			FIRST ORDER. RATE CONSTANT hr^{-1}
		1 hour	2 hours	3 hours	
NaO_2	207.7	78.1	98.1	100	0.690
NaO_2 + MnO_2	216.6	75.0	94.6	97.9	0.598
NaO_2 + CuPh(b)	189.7	97.9	100	100	3.069 1.218
NaO_2 + V_2O_3	229.5	81.0	98.0	≈100	0.713
NaO_2 + V_2O_5	221.8	67.4	90.1	97.8	0.534
NaO_2 Exposed to 100% Humidity for 15 Minutes	222.4	63.0	90.7	98.2	-----

(a) Theoretical O_2 = 305.5 ml/g for reaction $-2NaO_2 \longrightarrow Na_2O + 3/2\ O_2$ of 100% pure NaO_2 (256.6ml/g for 84% Purity)

(b) Polymeric Copper Phthalocyanine 2.

2.2.6 Results of Isothermic Kinetic Studies of The Decomposition of Sodium Peroxide

Because sodium peroxide is an intermediate in the decomposition of sodium superoxide, the catalysts that are most effective in increasing the oxygen production from the superoxide are those which facilitate the decomposition of sodium peroxide to sodium oxide. An investigation of the effects of those catalysts on the thermal stability of pure sodium peroxide, therefore, was carried out. Studies were conducted with three catalysts, manganese dioxide, copper polyphthalocyanine-2,and vanadium(III) oxide. The effects of the physical form of the peroxide were also examined by employing a compressed pellet of Na_2O_2 in addition to the usual powdered form. The results of the studies conducted at 250°C are summarized in Table VI. Analysis of the sodium peroxide used in this phase revealed that the superoxide content of the seemingly "pure" material was exceptionally high; greater than the 10% expected in commercial grade sodium peroxide.[19] The percent decomposition of sodium superoxide that occurred during the peroxide reaction being studied, therefore, was included in Table V.

The small amount of decomposition recorded for the peroxide pellet is immediately obvious. It appears that the surface area of the peroxide has a significant effect on the thermal decomposition. A similar effect was noted by Markowitz in studying the decomposition of lithium peroxide.[17]

As in previous studies, the manganese dioxide markedly increased the decomposition of the peroxide. An unexpected result, however, was the mild explosion encountered with the phthalocyanine catalyst. The reaction proceeded normally for the first three or four minutes and suddenly the sample ignited with a loud crack. The inside of the glass reaction vial was coated with a smokey gray substance typical of the combustion of a high molecular weight organic compound. This uncontrolled reaction presents conclusive proof that the phthalocyanine nucleus is susceptible to oxidative attack at this temperature.

TABLE VI

SUMMARY OF ANALYTICAL DATA FOR ISOTHERMAL
KINETIC STUDIES OF Na_2O_2 AT 250°C.

COMPOSITION OF SAMPLE	% CATALYST[(a)]	% NaO_2		% Na_2O_2		% Na_2O		% NaOH		% Na_2CO_3		PER CENT DE-COMPOSITION OF		DURATION OF RUN IN HOURS
		Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Na_2O_2	NaO_2	
Na_2O_2 (pure pellet)	0.0	4.1	4.9	84.4	83.7	0.0	0.0	11.1	11.3	0.6	0.0	0.83	--	6
Na_2O_2 (pure powder)	0.0	21.0	20.1	51.0	48.7	0.0	0.0	29.5	30.3	0.0	4.2	6.9	6.6	5
Na_2O_2 + MnO_2 (powder)	7.8	19.4	12.3	47.0	36.0	0.0	10.2	27.2	28.1	0.0	1.7	25.8	38.6	4.2
Na_2O_2 + CuPh[(b)]	9.7	19.0	← SAMPLE DETONATED →	46.1		0.0		26.6		0.0				
Na_2O_2 + V_2O_3	8.5	19.2	18.2	46.7	42.0	0.0	0.0	27.0	27.7	0.0	3.1	12.3	7.6	3

(a) % By Weight; (b) Polymeric Copper Phthalocyanine -2

The kinetic curves for the various peroxide samples are given in Figures 41-43. In all cases, essentially all of the oxygen is evolved in the first half hour. With the MnO_2 sample, the final volume of oxygen per gram of sodium peroxide is abnormally low. This catalyst gave the highest percent decomposition of peroxide, and yet the volume of oxygen evolved is approximately half of that obtained from the pure sodium peroxide. Again, the sample residue was bright blue, and, in all probability, the catalyst reacted, thus consuming a good portion of the oxygen.

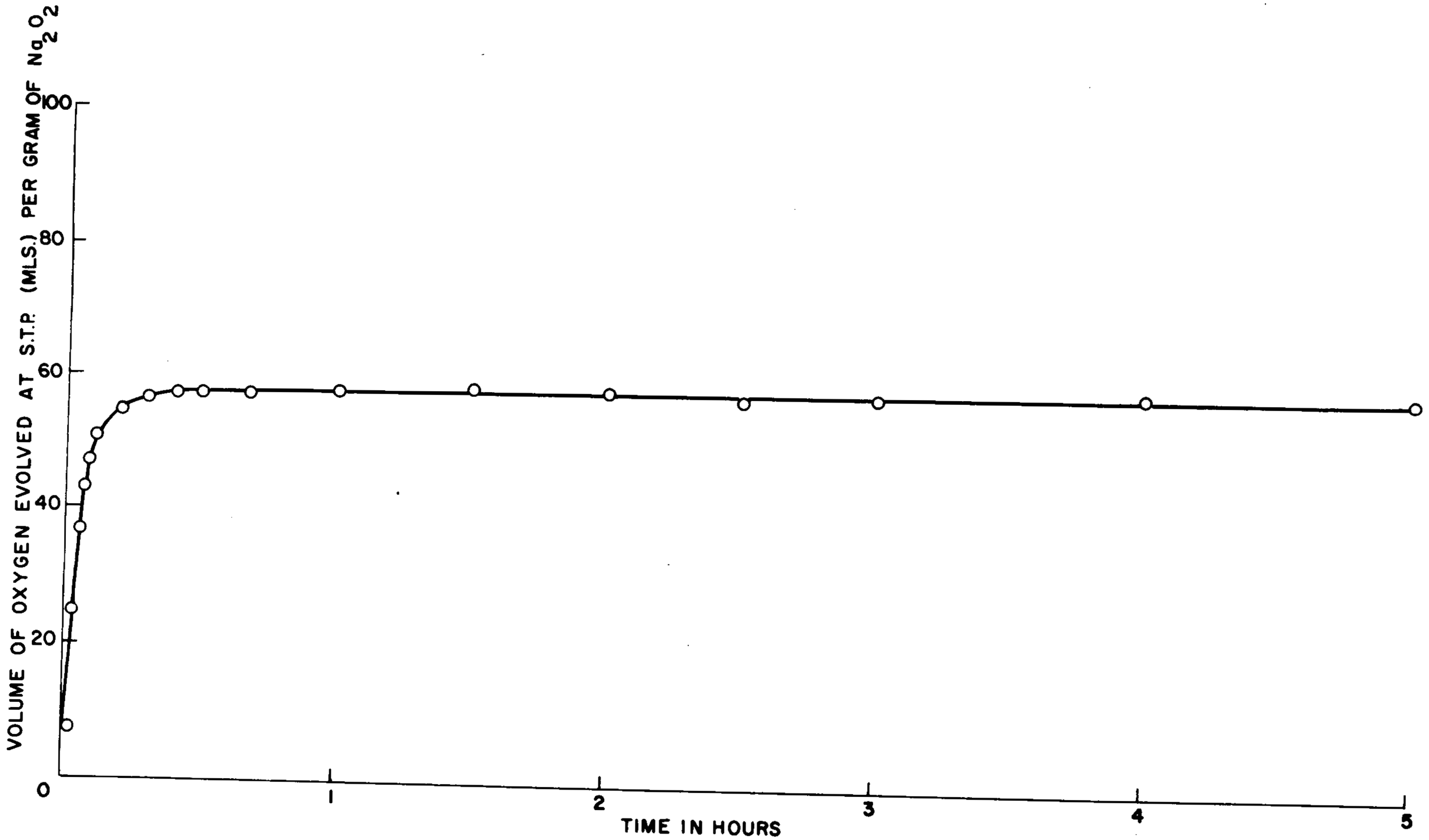


FIGURE 41 VOLUME OF OXYGEN EVOLVED AT STP PER GRAM OF POWDERED SODIUM PEROXIDE AT 250°C

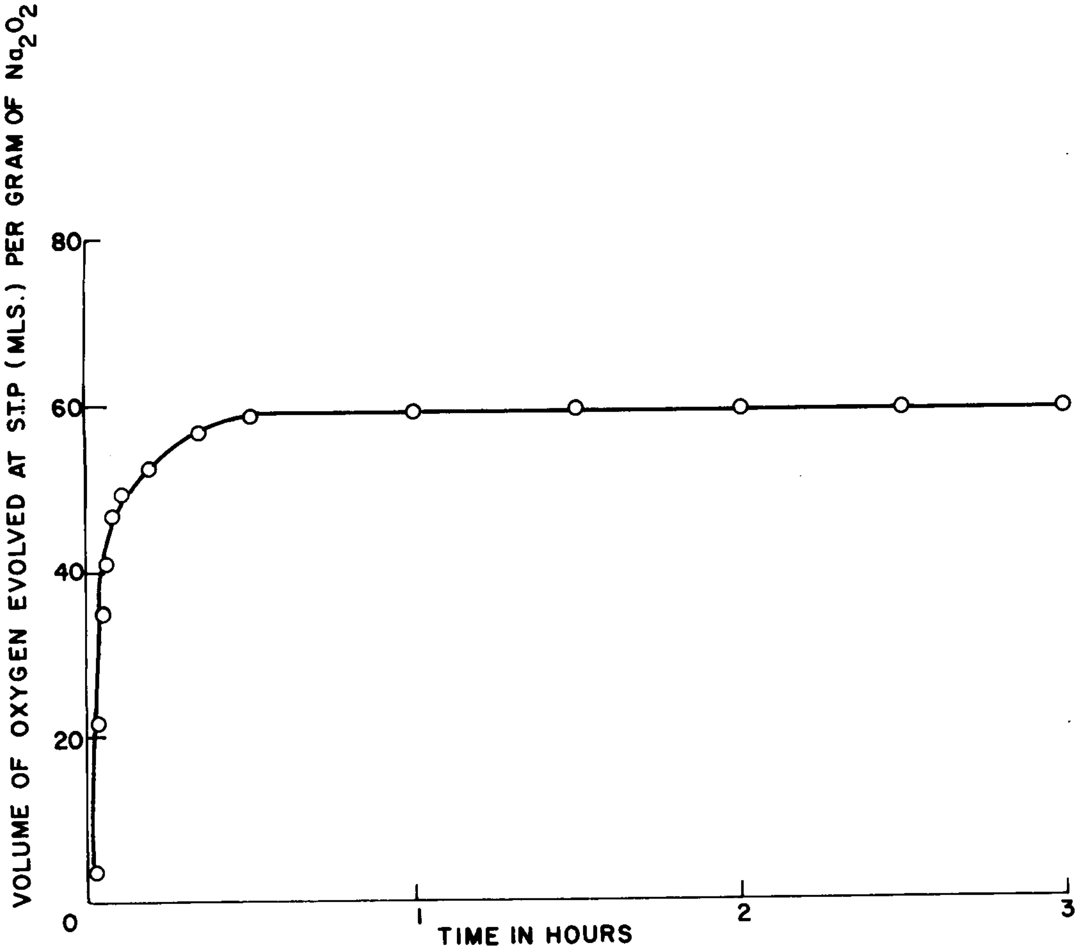


FIGURE 42 VOLUME OF OXYGEN EVOLVED AT STP PER GRAM OF Na_2O_2 IN A SAMPLE CONTAINING 46.7% Na_2O_2, 8.5% V_2O_3 AND 19.2% NaO_2 AT 250°C

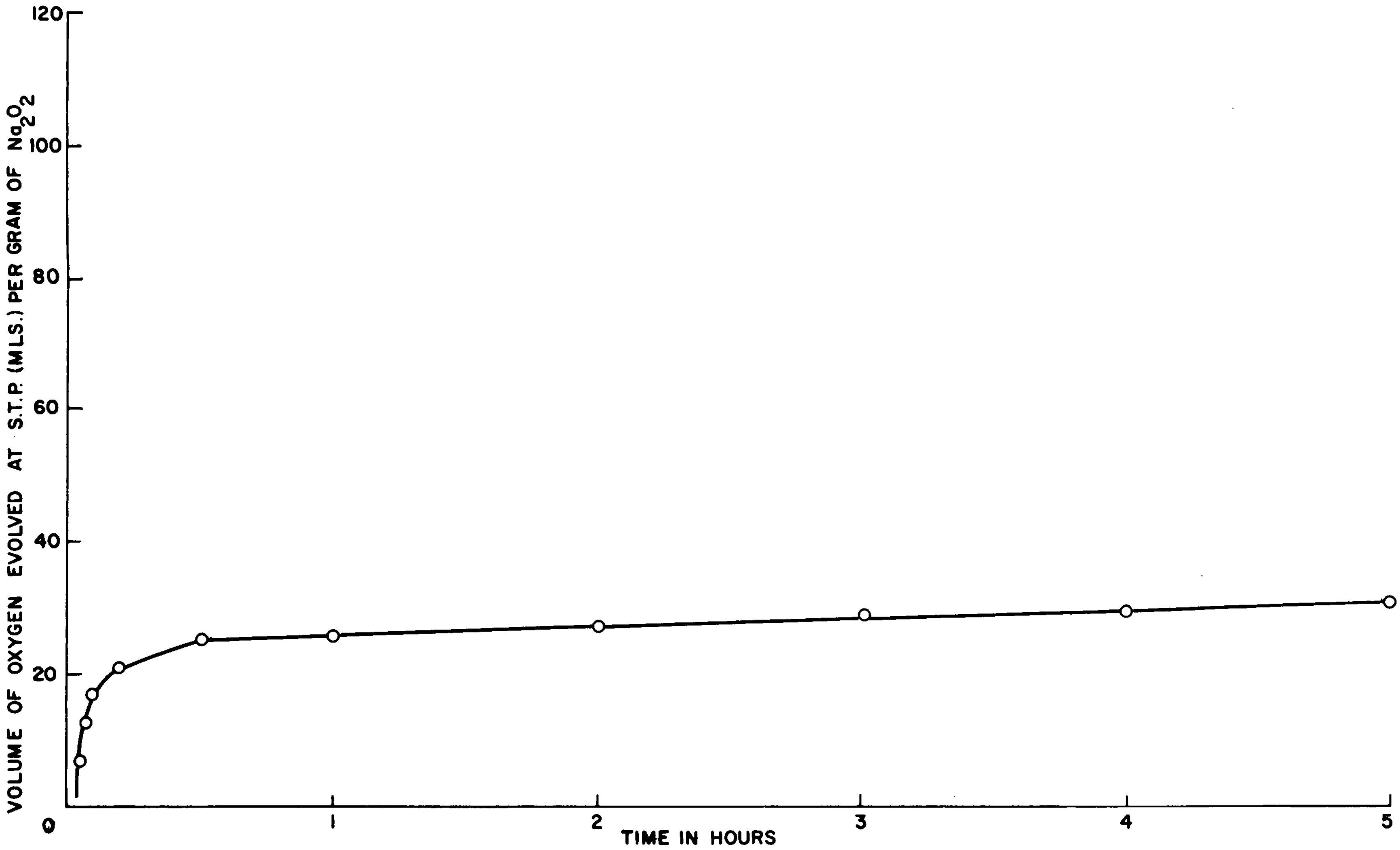


FIGURE 43 VOLUME OF OXYGEN EVOLVED AT STP PER GRAM OF Na_2O_2 IN A SAMPLE CONTAINING 47.0% Na_2O_2, 7.8% MnO_2 AND 19.4% NaO_2 AT 250°C

II

MAGNETIC SUSCEPTIBILITY OF CALCIUM SUPEROXIDE

1. INTRODUCTION

Magnetic susceptibility studies of calcium superoxide were continued to characterize more fully its magnetic and structural properties. In the interim report, results for only one temperature were reported. During the extended work period, measurements were made at temperatures ranging from -170 to 38°C, to determine the paramagnetic Curie-temperature, or Curie-point. Using these data, a more accurate permanent magnetic moment could be determined. Consequently, a more accurate independent analytical check for the presence and purity of superoxides could be made.

Previously reported magnetic data for calcium superoxide were obtained with low purity samples (2-5%[20]). The availability of higher purity samples (nearly 50%) for this work provided the opportunity to define more clearly the magnetic properties of calcium superoxide.

2. EXPERIMENTAL PROCEDURE

The Gouy apparatus and experimental procedures used have been described in the recent interim report.[1] However, the low temperature measurements required a special apparatus to maintain the sample tube at a constant temperature. This apparatus in shown in Figure 44. Using a constant flow of dry nitrogen gas, constant equilibrium temperatures were readily attained within 0.5 to 1 hour. The following baths were used to obtain the corresponding temperature: ice bath: 11°C; 30g $CaCl_2$/100g snow: 0°C; dry ice/acetone: -64°C; liquid nitrogen: -178°C.

Since measured gram susceptibilities are affected by the presence of diamagnetic impurities, corrections were made for: CaO_2 ($-0.33 \cdot 10^{-6}$ c.g.s.units), $CaCO_3$ ($-0.38 \cdot 10^{-6}$ c.g.s.units), $Ca(OH)_2$ ($-0.30 \cdot 10^{-6}$ c.g.s.units), and H_2O ($-0.70 \cdot 10^{-6}$ c.g.s.units).[21]

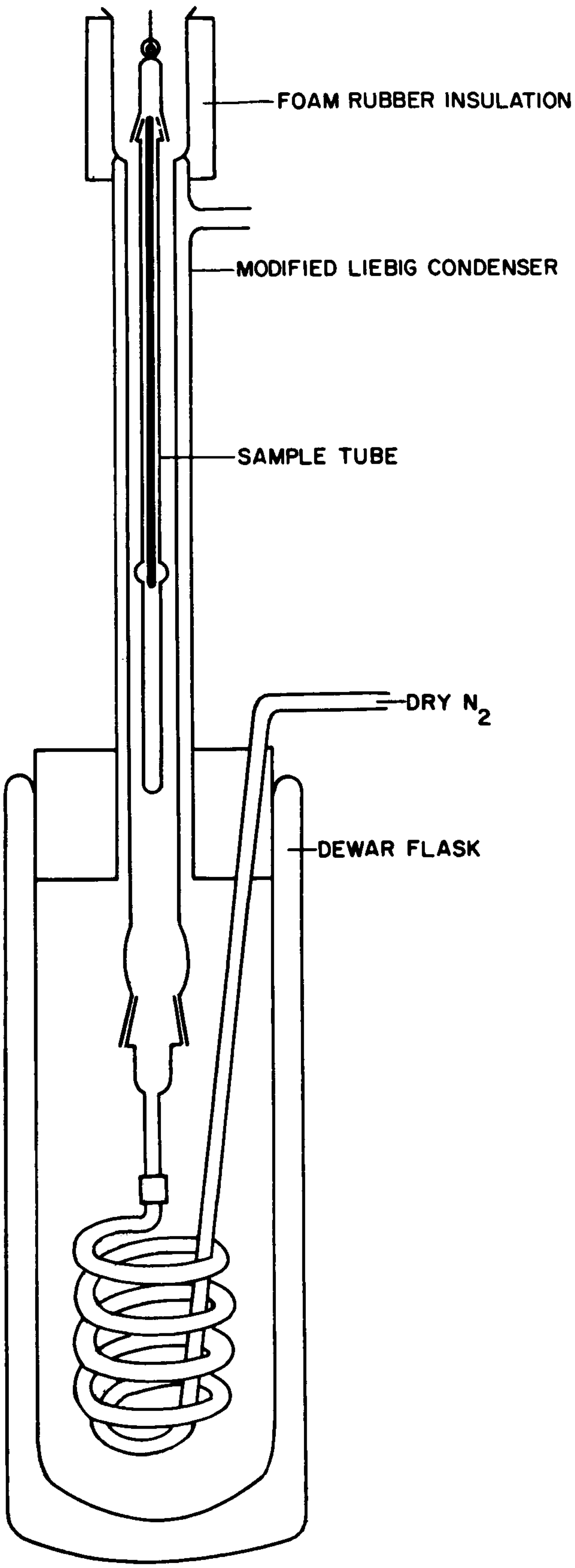


FIGURE 44 APPARATUS FOR MAGNETIC SUSCEPTIBILITY MEASUREMENTS AT LOW TEMPERATURES

Since these values are not affected by changes in temperature, the total diamagnetic values for each sample, calculated from Weidemann's additivity law, remained constant for a given sample at any temperature.

3. RESULTS OF MAGNETIC SUSCEPTIBILITY MEASUREMENTS

Magnetic susceptibility measurements of $Ca(O_2)_2$ samples of 20.0% and 48.0% purity were made at +38, +28, +11, 0, -64, and -178°C and are summarized in Table VII. The gram susceptibility of the pure sample at each temperature was obtained by extrapolating to 100% purity, the curve derived by plotting the measured gram susceptibility vs. composition (Figure 45). These results, summarized in Table VIII, were used to construct a plot of the reciprocal of the molar susceptibility (χ_m) of $1/2Ca(O_2)_2$ vs. the absolute temperature (Figure 46). The straight line was observed to intersect the T-axis at 0°K (Curie-point) indicating that for the temperature range studied, -178 to +38°C, the Curie Law was obeyed for calcium superoxide. The reciprocal of the slope of this line, equal to the Curie constant $[C_m = \chi_m(T-\theta)]$, was found to be $0.418^{\circ}K\ c.g.s.^{-1}$, which yields a molar susceptibility of 1400.10^{-6} c.g.s. units at 25°C and a permanent magnetic movement (μ_B) of 1.84 Bohr magnetons. This latter value is in excellent agreement with the theoretical value of 1.85 for the $^2\Pi$ state for O_2^- [22], Table VIII.

4. DISCUSSION OF RESULTS

Since the superoxide anion, O_2^-, is the only source of the paramagnetism and exists as an independent ionic unit in the superoxide crystal lattice, the molar susceptibility may be halved to obtain the value for one O_2^- unit in the $Ca(O_2)_2$ biradical.

In addition, the Curie constant should hold true for any superoxide system. Thus, using a value of $\chi_m = 1710 \cdot 10^{-6}$ c.g.s. units, a Curie-point of +51°K is calculated for potassium superoxide, Table IX. This value assumes that since the O_2^- anion is the only source of the paramagnetism and because the alkali and the alkaline earth

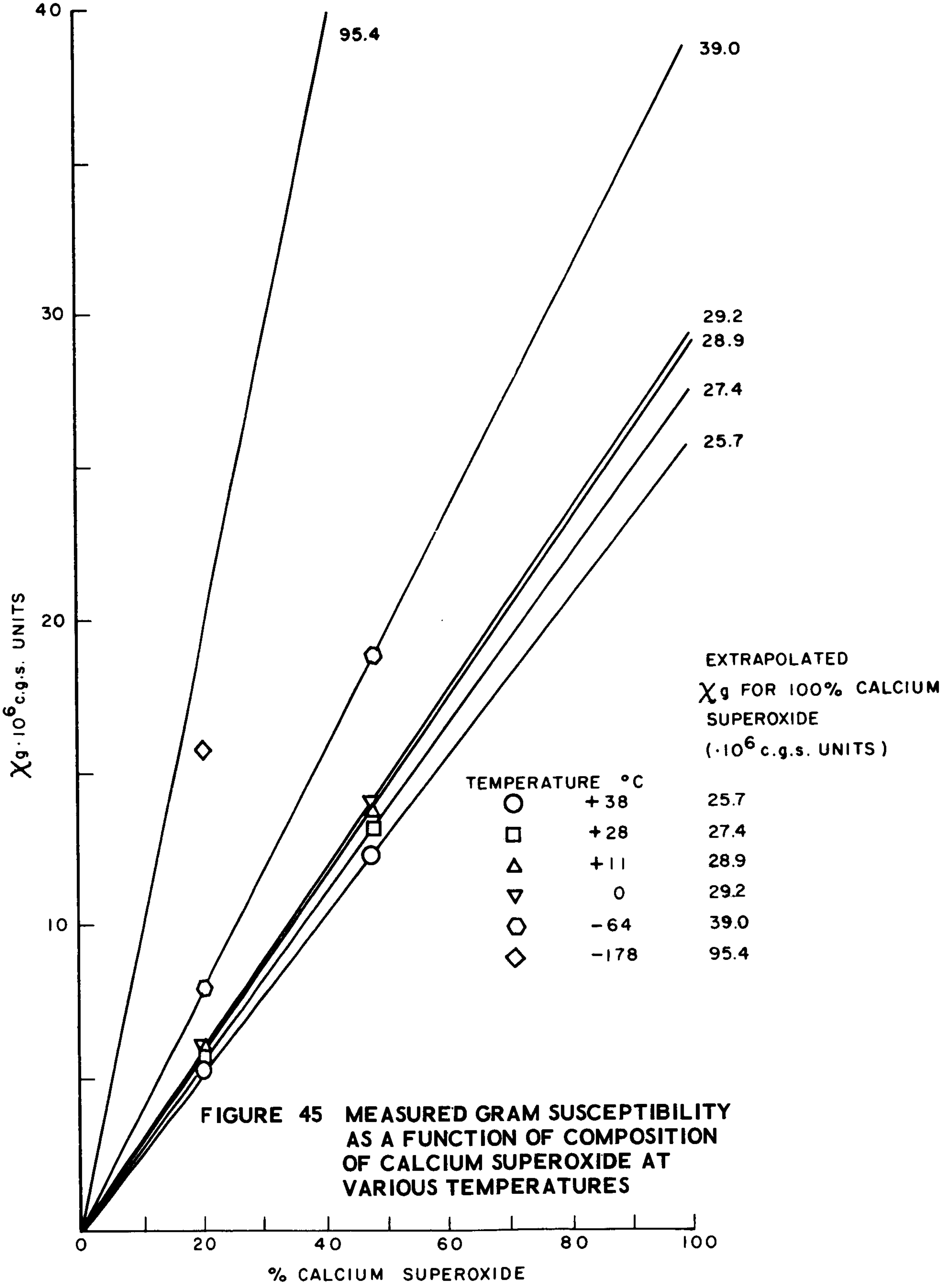


FIGURE 45 MEASURED GRAM SUSCEPTIBILITY AS A FUNCTION OF COMPOSITION OF CALCIUM SUPEROXIDE AT VARIOUS TEMPERATURES

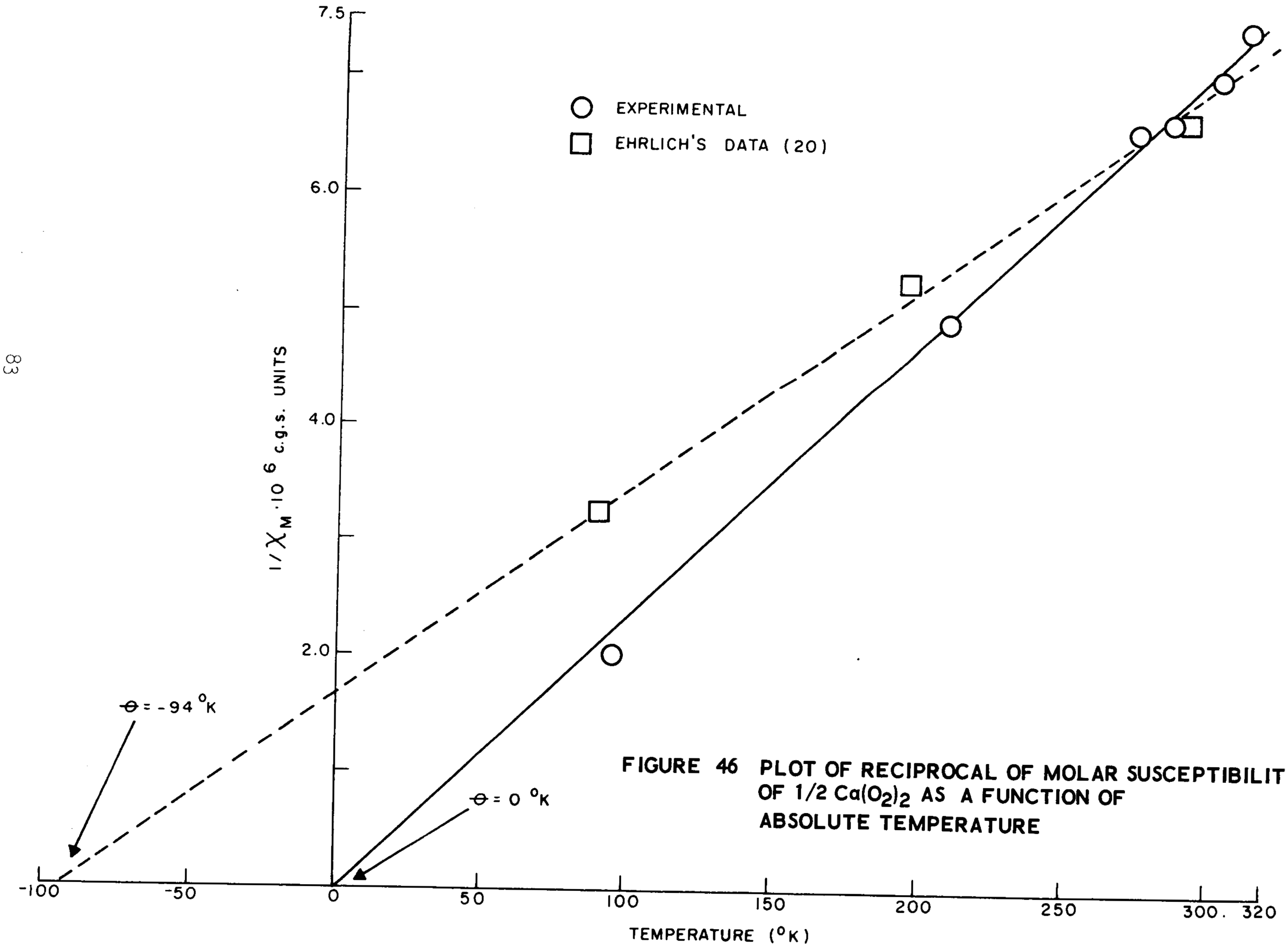


FIGURE 46 PLOT OF RECIPROCAL OF MOLAR SUSCEPTIBILITY OF 1/2 $Ca(O_2)_2$ AS A FUNCTION OF ABSOLUTE TEMPERATURE

TABLE VII

SUMMARY OF MAGNETIC SUSCEPTIBILITY MEASUREMENTS FOR CALCIUM SUPEROXIDE SAMPLES AT VARIOUS TEMPERATURES

COMPOSITION % wt. $Ca(O_2)_2$	TEMPERATURE (^{o}C)	GRAM SUSCEPTIBILITY ($\chi_g \cdot 10^6$ c.g.s.units)	
		Measured	Corrected[(a)]
48.0	+38	12.08	12.25
	+28	12.94	13.11
	+11	13.55	13.72
	0	13.68	13.85
	-64	18.71	18.88
	-178	49.66	49.83
20.0	+38	4.96	5.23
	+28	5.42	5.69
	+11	5.70	5.97
	0	5.70	5.97
	-64	7.68	7.95
	-178	15.40	15.67

(a) corrected for diamagnetic impurities using Weideman's law of additivity.

TABLE VIII

MOLAR SUSCEPTIBILITY OF CALCIUM SUPEROXIDE AT VARIOUS TEMPERATURES

TEMPERATURE (°C)	SUSCEPTIBILITY ($\cdot 10^6$ c.g.s.units)		
	GRAM[(a)] (χ_g)	MOLAR (χ_m)	1/2 MOLAR ($1/2\,\chi_m$)
38	25.7	2680	1340
28	27.4	2850	1420
11	28.9	3010	1500
0	29.2	3040	1520
-64	39.0	4060	2030
-178	95.4	9930	4960

(a) obtained by extrapolation to 100% $Ca(O_2)_2$, Figure 45.

TABLE IX

SUMMARY OF MAGNETIC PROPERTIES OF CALCIUM AND POTASSIUM SUPEROXIDES

COMPOUND	REFERENCE	PURITY (%)	TEMPERATURE (^oC)	SUSCEPTIBILITY $\chi \cdot 10^6$ c.g.s.units		CURIE CONSTANT (C_m ^oK c.g.s.$^{-1}$)	CURIE POINT (^oK)	MAGNETIC MOMENT (Bohr magnetons)	
				GRAM	MOLAR			effective	permanent
1/2Ca(O_2)$_2$	Experimental	20-48	25	13.4	1400	0.418	0	1.84	1.84
	Ehrlich[20]	2-5	17	13.5(a)	1400	0.535	-94	1.8	2.1
KO_2	Experimental	85	22	24.1	1710	0.418	+51	2.02	1.84
	Ehrlich[20]	---	20	22.9	1630	0.502	-15	1.96	2.01
	Neyding and Kazarnovskii[22]	---	20	25.01(a)	1778	0.434(a)	+51	2.05	1.87(a)
	Neumann[23]	---	20	24.2(a)	1720	0.420(a)	+51	2.02(a)	1.84(a)
Theoretical for Single Unpaired Electron	$^2\Pi$ State[24]	---	25	---	1420	0.423	---	---	1.85
	Spin effect only[1]	---	25	---	1240	0.371	---	---	1.73

(a) calculated from reported values

metal cations are only weakly diamagnetic, the Curie constant for various highly concentrated superoxide compounds should be essentially the same. The permanent magnetic moment for KO_2 was thus found to be 1.84.

Comparison with Ehrlich's data[20] showed excellent agreement for the measured gram susceptibility at room temperature. However, at the lower temperatures, considerable differences in results were observed, probably because Ehrlich employed very dilute samples for his studies[20]. The corrections for the diamagnetic impurities in the present work were usually very small, and, in samples with very high superoxide content, they were nearly negligible, e.g., approximately 5% correction for diamagnetic impurities for 20.0% $Ca(O_2)_2$ and less than 1% for 48.0% $Ca(O_2)_2$. By comparison, Ehrlich's diamagnetic corrections for calcium peroxide were proportionately very large, greater than 90% in some cases. As a result, Ehrlich calculated a permanent moment of 2.1 Bohr magnetons, compared to the value of 1.84 Bohr magnetons reported in this work.

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SUMMARY

The work completed during this phase of Contract NASw-559 can be summarized as follows:

1. Differential thermal analysis and thermogravimetric studies have been performed on pure samples of sodium superoxide, sodium peroxide, and lithium peroxide, and on samples of these materials containing various metallic oxide and metallo-organic catalysts.

2. Differential thermal analysis has demonstrated that sodium peroxide begins to decompose at ca. 310°C, and that above 350°C the decomposition is rapid. Lithium peroxide decomposes in the temperature range from about 310 to about 380°C. The decomposition of all three of these compounds are endothermic processes.

3. The addition of metallic oxide or metallo-organic catalysts to sodium superoxide, sodium peroxide, or lithium peroxide failed to decrease the temperatures at which the compounds decomposed. Differential thermogravimetric data, however, have shown that the addition of 1% cuprous oxide to sodium superoxide causes a slight increase in the rate of thermal decomposition.

4. Isothermal kinetic studies were performed on pure and catalyzed samples of sodium superoxide and sodium peroxide. Based on DTA data, reaction temperatures were set at 160 and 250°C. Catalysts included in this study were manganese dioxide, vanadium(V) oxide, vanadium(III) oxide, aluminum oxide, and copper polyphthalocyanine.

Analytical data obtained from the thermal decomposition products of sodium superoxide studies indicate that the degradation takes place in two distinct steps: (1) the conversion of superoxide to peroxide and oxygen and (2) the decomposition of peroxide to give the oxide and additional oxygen.

At both 160 and 250°C, sodium superoxide decomposed to form principally sodium peroxide with only a small amount of sodium oxide being produced. At 160°C the decomposition proceeded to 41.4% of completion in 140 hours while at 250°C, 87.2% of completion was achieved in 7 hours.

At the lower temperature, two catalysts, vanadium(V) and vanadium(III) oxides appeared to accelerate the decomposition of superoxide. The higher oxidation state facilitated the superoxide-peroxide transition with no oxide being formed, while the vanadium(III) compound catalyzed the conversion of superoxide all the way to the oxide. Another catalyst, manganese dioxide, also increased the amount of oxide formed, although the percent of superoxide converted was somewhat less than that obtained with pure sodium superoxide.

5. At 250°C, all of the catalysts tested appeared to retard the conversion of sodium superoxide to sodium peroxide. It is postulated that complexes of the general type, $NaO_2 . M_xO_y$, are formed. The complexes are considered to decompose at a slower rate than the uncomplexed sodium superoxide, thus accounting for the apparently lower conversion to the peroxide. Manganese dioxide and copper phthalocyanine effectively catalyze the decompostion of the uncomplexed superoxide completely to the oxide and oxygen.

6. Studies were conducted on the thermal decomposition characteristics of sodium superoxide samples preconditioned by exposure of atmospheres of 100% relative humidity for varying periods of time. Such conditioning appeared to lower slightly the onset of thermal decomposition. The rate of decomposition was not significantly affected by preconditioning with moisture.

7. Magnetic susceptibility measurements were made at 38, 28, 11, 0, -64, and -178°C for calcium superoxide samples of 20.0 and 48.0% purity. The Curie-temperature was determined to be 0°K indicating that the Curie Law was obeyed. The molar susceptibility for calcium

superoxide was calculated to be $2850 \cdot 10^{-6}$ c.g.s. units at 24°C. The permanent moment for $1/2Ca(O_2)_2$ was calculated to be 1.84 Bohr magnetons which is in excellent agreement with the predicted theoretical value.

CONCLUSIONS

The potential uses of alkali metal ozonides and superoxides, as well as calcium superoxide, as air revitalization materials have been the subject of studies conducted under NASA Contract NASw-559 since February, 1963. The results of this research and the problems associated with the synthesis and chemical characterization of these compounds have been presented in the reports submitted as partial fulfillment of the subject contract.

A summary of active chemicals, their availability, adaptability to long or short duration space missions, and experience factors concerning their application as air revitalization materials is given in Table X.

The studies concerned with alkali metal ozonides clearly established the potential of these materials for use in non-regenerative air revitalization systems. Oxygen production resulted from the reaction of water (vapor) with the ozonide and yielded the corresponding hydroxide which was capable of absorbing carbon dioxide. The attractiveness of this system was further enhanced by the fact that bicarbonates were formed upon reaction with carbohydroxide, thus resulting in favorable respiratory quotients.

Potassium ozonide was successfully prepared in greater than 95% purity but in only small (10%) yields. The stoichiometries of the pertinent chemical reactions for potassium ozonide as well as its thermal stability properties were characterized. The present inability to prepare large-scale quantities of potassium ozonide, however, and the difficulties encountered in synthesizing sodium ozonide prevent the consideration of the alkali metal ozonides as "off-the-shelf" items, i.e., ready for use. It is necessary, therefore, that continued efforts be expended for fundamental studies in the areas of the synthesis and engineering of these materials for air revitalization systems.

SUMMARY OF ACTIVE CHEMICA

Active Chemical	Formula	Availability	Adaptability to Life Support Syst
Sodium Superoxide	NaO_2	Commercially available. >95% purity. Currently expensive ($20/lb).	May be considered suitable in chemi air revitalization system to supply oxygen and remove carbon dioxide ar noxious and toxic airborn contamina Present state-of-the-art indicates material suitable for missions of 135 to 180 man-days in length. Lor term storage stability is an attrac asset. Potentially the best of the currently considered non-regenerati systems in terms of weight and volu requirements.
Potassium Superoxide	KO_2	Commercially available. >95% purity. ($2/lb)	Same as for sodium superoxide but less oxygen storage capacity. Ada for space missions of up to 95 man in length.
Calcium Superoxide	$Ca(O_2)_2$	Laboratory quantities only, purities up to 60%.	If available in purities greater t 90%, would be superior to the alka metal superoxides in all regards a would, in addition, offer attracti potential in a back-pack unit.
Lithium Peroxide	Li_2O_2	Commercially available. >85% purity. ($18/lb)	Both CO_2 scrubber and oxygen sourc greater CO_2 capacity than lithium hydroxide. Catalyst necessary for complete re with water vapor and CO_2.
Sodium Ozonide	NaO_3	Laboratory quantities only. >90% purity reported. Current laboratory synthesis techniques not suitable for large scale production.	Would be useful as multi-purpose c pound for supply of oxygen, remova carbon dioxide, and noxious and to air-born contaminants.
Potassium Ozonide	KO_3	Laboratory quantities only. >90% purity in low yield. Current laboratory synthesis techniques not suitable for large scale production.	Same as for sodium ozonides but wi less oxygen storage capacity and greater thermal stability.
Sodium Peroxide	Na_2O_2	Commercially available. >90% purity. Fluff material ($0.95/lb) Pellet material ($0.21/lb)	Potentially useful as an auxiliary primary CO_2 scrubber, however, not attractive as lithium peroxide com for these purposes, nor in terms o oxygen storage capacity.
Potassium Peroxide	K_2O_2	Not commercially available.	None
Lithium Superoxide	LiO_2	Not available Numerous attempts at synthesis unsuccessful. Reported successes questionable. Thermodynamic studies show it to be unstable at useful temperatures.	Would be outstanding active chemic for oxygen supply.
Lithium Ozonide	LiO_3	Not available. Unfavorable thermodynamics. No reports regarding possible synthesis.	Would offer greatest oxygen storag capacity of all active chemicals.

TABLE X

LS FOR USE AS AIR REVITALIZATION MATERIALS

em	Experience Factors Related to Space Cabin Use	Status As Air Revitalization Material
cal d nts. this p to g tive ve me	Successful laboratory evaluations (GD/EB and others), manned chamber tests (Boeing), may possibly have been the chemical of choice in Russian animal and manned space flights.	Ready for use pending design and test of an actual flight system.
ith table days	Extensive studies both in USA and USSR. Was in all probability the chemical of choice in the Soviet manned and animal space flights.	Same as for sodium superoxide.
an i d e	Limited laboratory studies on synthesis and characterization as an air revitalization material (GD/EB, ONR, Soviets).	Requires continuation of basic studies to develop a method of producing this compound in purities greater than 90% and on a large scale.
, ction	Some laboratory studies on synthesis and utilization as air revitalization material (Foote Mineral Company).	Mechanisms and control of pertinent air revitalization reactions not completely known. Long term basic chemical and engineering studies required (2 to 3 years) in order to insure its reliability in space missions.
m- of ic	Some laboratory studies on its synthesis and evaluation as air revitalization material (GD/EB, IIT, and Soviets).	Will require long-term basic studies (2 to 3 years) to resolve problems of its synthesis on large scale and the problem of thermal stability.
h	Same as for sodium ozonide.	Same as for sodium ozonide except for thermal stability.
or as ound	Limited information available. Some laboratory studies.	Doubtful value for space cabin applications based on water vapor reactions. Of value when admixed with sodium superoxide for specially-designed water reactors.
	None	None
l	None	None
	None	None

In the recent interim report[1], it was concluded that the chemistry of sodium and potassium superoxides has been sufficiently developed to allow the application of these materials in air revitalization systems. The reactions of these compounds with water vapor and carbon dioxide have been extensively studied. In a semi-passive unit, designed for use in closed environments such as space cabins, the desired respiratory quotient may be readily maintained by proper control of flow rates and levels of humidity. The usefulness of these compounds, moreover, has been ably demonstrated by the following: the microcontactor (using potassium superoxide) developed at General Dynamics, Electric Boat division, under the auspices of NASA[27]; the five-man test (employing sodium superoxide) successfully completed by the Boeing Aircraft Co. under the direction of NASA[28,29]; the atmosphere control unit (using potassium superoxide discs) designed and fabricated by the MSA Research Corporation in cooperation with the Aerospace Medical Division of Wright-Patterson Air Force Base[30]; the company-sponsored efforts of the General Dynamics, Electric Boat division, in developing a "Potassium Superoxide Air Revitalization System" for small submersibles[31]; and the dramatic use of sodium or potassium superoxide in the Russian Vostok and Voskhod manned flights[32,33,34]

The weight and volume characteristics of an air revitalization system based on the reaction of water vapor with sodium or potassium superoxide are compared in Table XI with other technically advanced, non-regenerative systems for a 90-day manned mission. These estimates, based on the analysis of available engineering data[31,35,36], assume the requirements of a 154-lb. man at moderate activity (an oxygen requirement of 1.87 lb./man-day, and a carbon dioxide output of 2.11 lb/man-day). Weight estimates for three-man capacity systems have been shown to range from 280 to 600 pounds[37,38]. Estimated

TABLE XI

Weight and Volume Characteristics for Advanced State-of-the-Art, Non-Regenerative Air Revitalization Systems

System	Fixed Weight (lbs.)	90 Man-Day Mission Total Weight (lbs.)	Fixed Volume (cu. ft.)	90 Man-Day Mission Total Volume (cu. ft.)
LiOH (alone)	12	269	2	8
LOX (150 psi) (50% Loss)	20	209	1	11
O_2 Spheres (3000 psi)(SAE 4340 Steel, Safety Factor 1.88)	10	534	1	13
LOX (50% Loss)/ LiOH	32	667	3	19
O_2 Spheres/LiOH	22	803	3	21
KO_2	12	769	2	17
NaO_2	12	598	2	13.5

(Fixed weight and fixed volume estimates include blowers, manifolds, regulators, control device, and miscellaneous piping and tubing.)

power requirements for regenerative systems are on the order of two kilowatts. Since a realistic weight-to-power ratio is generally assumed to be 300 lbs. per kilowatt, approximately 600 lbs. must be added to the basic estimated weight of the regenerative systems. The estimated power requirement of non-regenerative systems is on the order of only 0.1 kw, and only 30 lbs. for power supply need be added to their basic system weight.

A comparison of system weights, including power supply weights, as a function of mission length is shown in Figure 47, while Figure 48 illustrates volume penalties as a function of mission length. These figures indicate that an active chemical system employing sodium superoxide offers the least weight and volume penalty of any of the non-regenerative systems considered and is clearly competitive with regenerative systems up to 125 to 180 man-days in length.

A number of the characteristics of a superoxide chemical air revitalization system which offer additional advantages to be considered in a trade-off study are not included in the above weight-volume-mission length comparisons. These advantages include control of cabin relative humidity, removal of air-borne bacteria and odoriferous human body waste products from the cabin atmosphere (thus offering possible reduction or elimination of auxiliary systems for removal of toxic contaminants), and the simplicity and reliability of operation compared to other candidate air regeneration systems.

For small, self-contained air revitalization units such as might be associated with space suits, extra-vehicular activities, and the like, canister-like devices must be employed. In these applications, however, the use of sodium or potassium superoxide is restricted by the crusting problem encountered with the alkali metal superoxide-water vapor canister reactions. In an attempt to circumvent this problem, calcium superoxide was investigated as an air

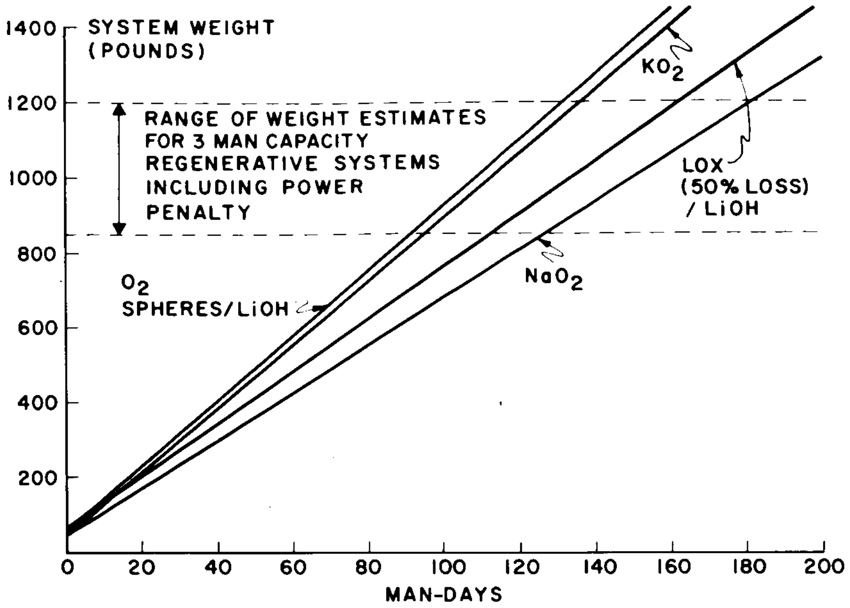


FIGURE 47 WEIGHT PENALTIES VS MISSION LENGTH FOR SELECTED NON-REGENERATIVE AIR REVITALIZATION SYSTEMS

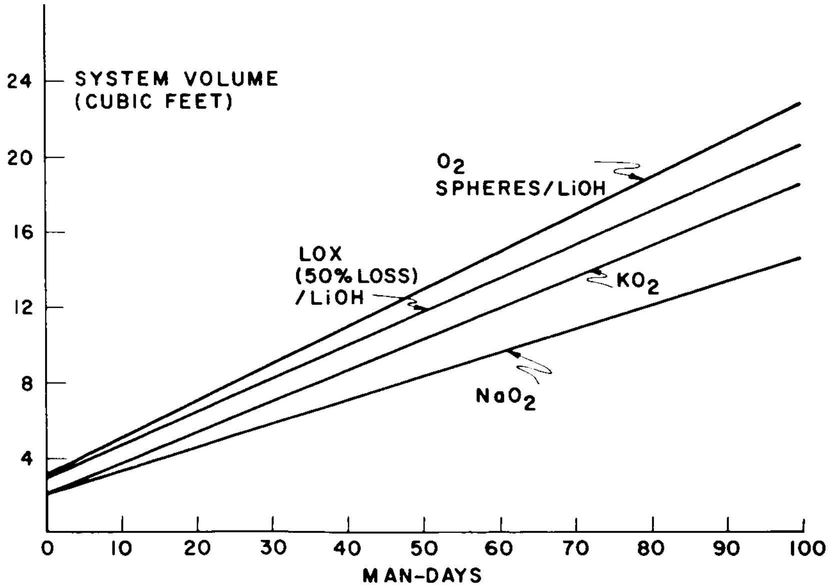


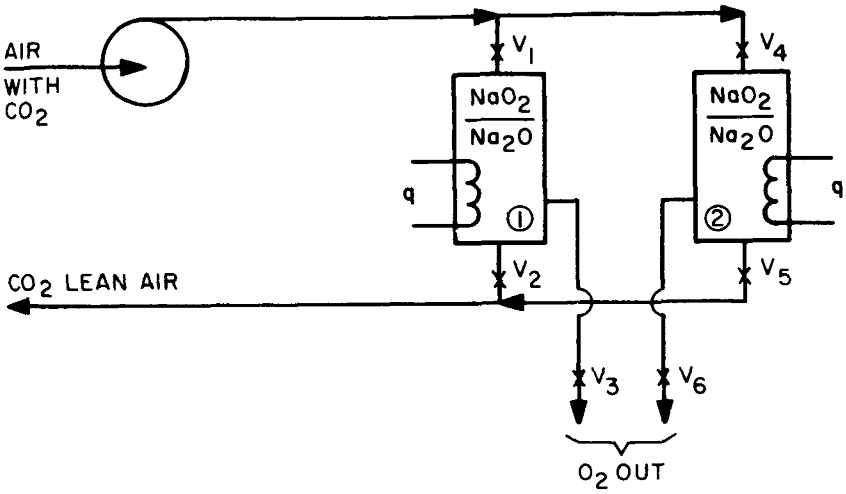
FIGURE 48 VOLUME PENALTIES VS MISSION LENGTH FOR SELECTED NON-REGENERATIVE AIR REVITALIZATION SYSTEMS

revitalization material. The interim report[1] concluded that calcium superoxide was not yet competitive with alkali metal superoxides because of the complexity of the reactions of calcium superoxide with carbon dioxide and water vapor. Before calcium superoxide can be considered for use in air revitalization applications, therefore, the pertinent reaction stoichiometries must be established, and the problems related to large scale synthesis of high-purity material must be resolved.

The present work was concerned with the investigation of an alternate to the superoxide-water vapor reaction. The determination of the thermal decomposition characteristics of sodium superoxides, sodium peroxide, and lithium peroxide has confirmed the feasibility of oxygen production through thermal activation of these air revitalization chemicals. Significant yields and rates of oxygen evolution from sodium superoxide can be obtained at elevated temperatures (near 250°C) in the presence of a suitable catalyst (e.g. V_2O_3). Pretreatment of the superoxide sample by exposure to moisture has been shown to lower slightly the temperature of thermal decomposition.

It has been demonstrated that the chemical best suited for these purposes would be sodium superoxide. Lithium peroxide cannot be considered at this time because it decomposes at a somewhat higher temperature (greater than 300°C) than sodium superoxide. Because of the elevated temperatures needed to effect decomposition, the use of sodium superoxide to produce oxygen via a thermal decomposition mechanism in a small, self-contained air revitalization unit does not appear encouraging at this time.

One conceptual design for an air revitalization unit based on the thermal decomposition of sodium superoxide is shown schematically with various modes of operation in Figure 49. Internal heaters would be employed with the high density superoxide material. Based



1 V_1, V_2 OPEN, V_3, V_4, V_5 CLOSED ----- CO_2 REMOVAL
V_1, V_2 CLOSED, V_3, V_4, V_5 OPEN ---- O_2 GENERATION

2 V_4, V_5 OPEN, V_1, V_2, V_6 CLOSED --- CO_2 REMOVAL
V_4, V_5 CLOSED, V_1, V_2, V_6 OPEN ---- O_2 GENERATION

FIGURE 49 CONCEPTUAL SCHEMATIC FOR AIR REVITALIZATION UNIT BASED ON THERMAL DECOMPOSITION OF SODIUM SUPEROXIDE on this conceptual design, engineering estimates were made for a "quasi-trade-off" study assuming a 1% catalyst level and an operating temperature of 100°C (ideal compared to experimentally determined 250°C). The weight and volume penalties were calculated in the manner described above for a one-man system based on the thermal decomposition (via two reaction paths) of sodium superoxide, and are summarized in Table XII. Figures 50 and 51 illustrate systems weights and volumes as functions of mission length. A comparison of this data with Figures 47 and 48 indicates that the superoxide thermal decomposition system does not offer any significant weight or volume advantages over a system based on a superoxide-water vapor reaction.

At this time, it can be concluded that sufficient thermal data for high density alkali superoxides material is not yet available for reliable engineering "trade-off" studies. In addition, before such "trade-off" studies can be made, the necessary data must be obtained and studies of many additional superoxide-catalyst systems should be exhausted.

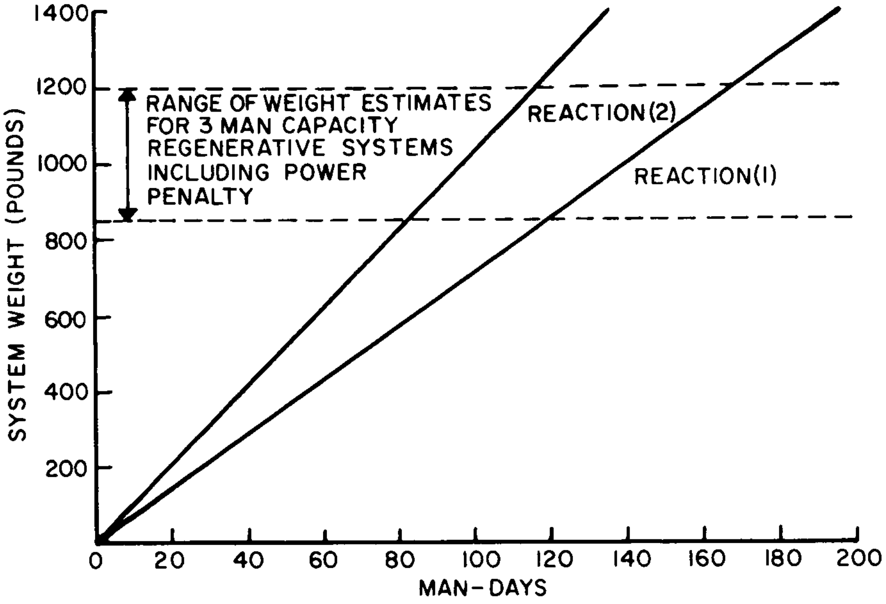


FIGURE 50 WEIGHT PENALTIES VS MISSION LENGTH FOR CONCEPTUAL NaO_2 THERMAL DECOMPOSITION AIR REVITALIZATION UNIT

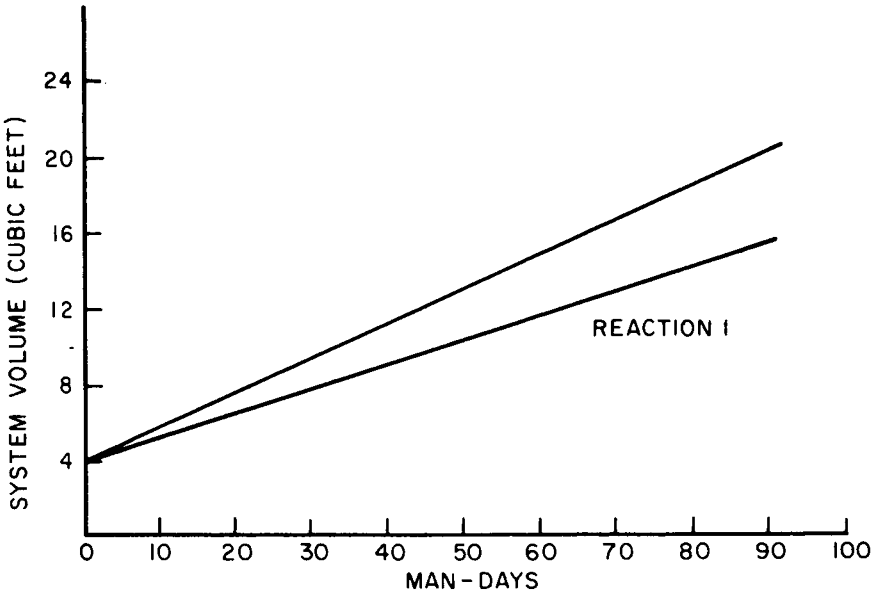


FIGURE 51 VOLUME PENALTIES VS MISSION LENGTH FOR CONCEPTUAL NaO_2 THERMAL DECOMPOSITION AIR REVITALIZATION UNIT

TABLE XII

Weight and Volume Characteristics for a Conceptual Non-Regenerative Air Revitalization System Based on the Thermal Decomposition of Sodium Superoxide

Reaction	No.	Power Requirements (watts)	Fixed Weight (lbs.)	90 Man-Day Mission-Total Weight(lbs)	Fixed Weight (cu. ft.)	90 Man-Day Mission Total Vol. (cu. ft.)
$2NaO_2 = Na_2O + 3/2\ O_2$	1	153	25	ca 630	4	16
$2NaO_2 = Na_2O_2 + O_2$	2	116	25	ca 930	4	21

(Fixed weight and volume estimates include blowers, manifolds, regulators, control device, and miscellaneous piping and tubing.)

RECOMMENDATIONS

It is recommended that:

1. A superoxide air revitalization system be designed and tested that would be oriented toward a specific space mission. It is recommended that the system be based on the reaction of either sodium or potassium superoxide with water vapor.

2. Studies of the thermal decomposition mode of activation for a superoxide air revitalization system be continued in order to make more reliable engineering trade-off studies compared to the water vapor mode of activation. Studies of various catalyst systems (particularly metal phthalocyanines and vanadium and copper oxides) with sodium and potassium superoxides should be continued in an effort to find a lower temperature of decomposition or faster rate of oxygen evolution. In addition, the feasibility of "on-off" type modes of operation by raising or lowering the applied thermal energy should be determined.

3. Basic studies related to the chemistry and synthesis of calcium superoxide be continued to develop a method of preparing this compound in at least 90% purities as well as in greater than laboratory quantities.

4. Long-term basic studies of alkali metal ozonides be continued to resolve problems concerning synthesis (particularly large scale production) and thermal stability.

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13 ABSTRACT

A study of the thermal stability of sodium superoxide, sodium peroxide, and lithium peroxide was conducted. The techniques of differential thermal analysis, thermogravimetry and differential thermogravimetry were used in evaluating the effects of metallic oxide and metallic-organic catalysts on the temperatures and rates of decomposition of these compounds. Results indicated that catalysts do not lower the thermal decomposition temperature but, in some cases, accelerate the rate of decomposition at a given elevated temperature. The effect of preconditioning sodium superoxide samples by exposure to humid atmospheres was also studied. Such conditioning lowers the decomposition temperature slightly. Isothermal kinetic data was also generated for a number of catalyzed systems. Magnetic susceptibility studies for calcium superoxides were extended to include measurements at temperatures ranging from -178 to 38°C.

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